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NAVORD REPORT 2705

THE THERMAL DECOMPOSITION OF NITROGUANIDINE

19 January 1953



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THE THERMAL DECOMPOSITION OF NITROGUANIDINE

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ABSTRACT: The gaseous products of the thermal decomposition of nitroguanidine have been quantitatively analysed. Nitrous oxide, ammonia, water and some carbon dioxide were found. Various properties of the thermal decomposition have been determined, and a mechanism for decomposition proposed. The kinetic rate equation for the thermal decomposition of nitroguanidine has been determined. It appears that the nitroguanidine surface is poisoned by either gaseous or solid decomposition products.

Explosives Research Department
U. S. NAVAL ORDNANCE LABORATORY
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This study was carried out under Task Assignment NOL-Re2d-02-1-53. The information developed is believed to be correct with regard to nitroguanidine alone. Its behavior in a propellant composition may be modified by the presence of other compounds.

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THE THERMAL DECOMPOSITION OF NITROGUANIDINE

INTRODUCTION

Nitroguanidine is a primary constituent of many so-called cool propellants. A study has been made of the thermal decomposition of nitroguanidine, in order to better understand the mechanism of the ignition of this type of propellant.

The thermal decomposition of nitroguanidine has previously been studied by Davis and Abrams (a). They devoted most of their efforts to an analysis of the solid residue and sublimate of the decomposition. This report deals primarily with the gaseous products of the decomposition and with the reaction kinetics of the system.

EXPERIMENTAL

1. Thermal Decomposition

Experiments on the thermal decomposition of nitroguanidine were carried out in the apparatus illustrated in Figure 1. A sample of nitroguanidine, which had previously been dried for two hours in a vacuum dessicator, was placed in tube A, a pyrex glass tube of approximately 8 mm. outside diameter. This tube was heated under vacuum for one-half hour previous to its use. The system from stopcock 2 to tube A was then evacuated for thirty minutes with a Hyvac pump, and a Dewar flask containing liquid nitrogen was placed around trap C. After stopcock 2 was closed, the system from stopcock 2 to tube A was under vacuum. An electric furnace at the desired temperature was then moved so that tube A fitted snugly within a heavy copper sheath within the furnace. See Figure 2. Time was measured from the moment the furnace surrounded the sample tube.

The gaseous products of decomposition are condensable at liquid nitrogen temperatures. The gaseous products were collected for a desired length of time in trap C, Figure 1, during which time a vacuum was drawn up to stopcock 1 through open stopcocks 3 and 4. A Dewar flask containing liquid nitrogen was next placed around trap B. Stopcock 3 was then closed, the time recorded, and stopcock 1 turned so that the gaseous products from A began to collect in trap B. Stopcock 5 was closed, and trap C, still surrounded by liquid nitrogen and containing condensed gaseous products, was removed from the system for analysis. A new trap was put in its place, and the process repeated. Thus about five gaseous samples, if desired, could be drawn from the thermal decomposition of one nitroguanidine sample.

Automatic temperature control was obtained by a Wheelco potentiostat through a chromel - alumel thermocouple described in Figure 2. Continuous temperature readings were facilitated by a Brown temperature recorder calibrated for a chromel - alumel thermocouple.

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2. Quantitative Analysis of Gaseous Products

a. Absorption Train for Gaseous Products

Trap C containing the condensed gaseous products was placed in an absorption train as described in Figure 3. Absorption tube A contained anhydrous, crystalline magnesium perchlorate, to remove ammonia and water quantitatively. Absorption tube B absorbed carbon dioxide and was filled two-thirds with ascarite, a sodium hydroxide-asbestos adsorbent mixture, and one-third with anhydrous. Trap D, which was surrounded by liquid nitrogen, condensed nitrous oxide. Absorption tubes E and F, containing anhydrous and ascarite respectively, were placed in front of the sample trap in the train in the usual fashion. Trap G surrounded by liquid nitrogen was employed as a safety for trap D to prevent oxygen in the air from diffusing to the latter trap. Helium rather than air was used as a flushing agent because oxygen is condensed at liquid nitrogen temperatures.

Before the sample trap was placed in the absorption train, the train was flushed with helium for one hour. Drawing air through the train by suction for 20 minutes, was followed by weighing the anhydrous and ascarite tubes, A and B, against respective tared tubes. The system was flushed with helium once again before the gaseous product trap C, still immersed in a Dewar flask containing liquid nitrogen, was placed in the train.

With the sample trap in the train and the Dewar flask removed, the system was swept with helium by pressure for 60 - 90 minutes depending on the size of the sample. At the end of this time, trap D, containing condensed nitrous oxide, was closed and removed from the system. An aspirator was attached to the train, and air was drawn through the system for 20 minutes in order to replace the helium. The tubes containing anhydrous and ascarite were then weighed against tares.

It was noticed that as the condensed gaseous products trap C warmed up after removing the cold trap, a white precipitate formed on the inside of the trap as room temperature was reached. The precipitate disappeared with time, and when the helium flushing was completed, no precipitate could be seen. This precipitate was believed to have been brought about by the combination of ammonia, carbon dioxide, and water.

b. Quantitative Analysis of Ammonia and Water

The combined weight of ammonia and water was obtained from the difference in the weight of the anhydrous tube. After weighing, the anhydrous (15 grams) was quantitatively transferred to an Erlenmeyer flask containing exactly 10 ml. of .1 N hydrochloric acid and 50 ml. of distilled water. To determine the amount of ammonia present, this solution was then back-titrated with .02 N sodium hydroxide solution using two drops of methyl red as an indicator. The anhydrous used was slightly basic, but its degree of basicity did not vary from sample to sample drawn from the same bottle. As an added precaution, a blank anhydrous sample was always taken along with a decomposition sample. Runs made with known amounts of ammonia proved the validity of this method of analysis. The amount of water in the anhydrous tube was obtained from the difference between the known combined weight of water and ammonia, and the calculated weight of ammonia.

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c. Quantitative Analysis of Carbon Dioxide

Carbon dioxide was calculated directly from the weight of the ascarite tube.

d. Quantitative Analysis of Nitrous Oxide

Cold trap D, Figure 3, containing gaseous helium and condensed nitrous oxide, was attached to a glass gaseous expansion apparatus. The system included an infrared cell, 10 cm. in length, which had rock salt windows. The cold trap, still surrounded by a Dewar flask containing liquid nitrogen, was pumped down to 10 mm. pressure of helium, and the Dewar flask was removed. Gaseous nitrous oxide was then allowed to expand into the evacuated infrared cell. After removing the cell from the system, air was let into the infrared cell till atmospheric pressure was reached.

Under atmospheric pressure, the infrared absorption of nitrous oxide is fairly insensitive to the presence of other gases. At a total pressure of the order of 30 mm., the infrared absorption of nitrous oxide is extremely sensitive to foreign gases (b). A calibration curve of $\log I_0/I$ vs. pressure of nitrous oxide at a total pressure of 760 mm. allowed us to calculate the pressure of an unknown sample of nitrous oxide from its absorption coefficient. The absorption of nitrous oxide was measured in a Perkin Elmer infrared spectrometer model #12C using a rock salt prism. The absorption band used was the doublet at 7.8μ that remained unresolved at a slit width of .080 mm.

The method of condensing nitrous oxide in the train was tested with known amounts of nitrous oxide and was shown to be analytical. An infrared spectrum from 2 - 15μ , using a double beam Perkin Elmer infrared spectrometer model #21, was taken of the gaseous products in the nitrous oxide cold trap D, Figure 3. No trace of ammonia was found.

In the kinetic studies of the thermal decomposition of nitroguanidine, it was only necessary to measure the amount of nitrous oxide evolved, since this was a measure of the amount of nitroguanidine decomposed. The procedure for the collection of nitrous oxide was the same as described above. Of course it was unnecessary to weigh the anhydrous and ascarite absorption tubes.

3. Infrared Spectrum of Solids

The infrared spectrums of some solid samples were taken using the double beam Perkin Elmer model 21 spectrometer. The solid samples were ground in a mortar, and a "mull" was prepared with nujol. Rock salt faces were used. Very often a blank sample using just the suspending oil was placed in the reference beam of the double beam spectrometer to compensate for the absorption of the nujol.

4. Materials Used

The nitroguanidine used in the experiments was Eastman Kodak White Label nitroguanidine. Unless otherwise specified, this material was used in a form that is described below as "ground nitroguanidine crystals". A list is given below of various species of nitroguanidine used in this research. The species will henceforth be referred to by the name in quotations.

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"ground nitroguanidine crystals": nitroguanidine that was ground in a Fisher Motor-Driven Mortar Grinder for two hours and had a powdery appearance.

"needle-like nitroguanidine crystals": nitroguanidine that had been re-crystallized from aqueous solution three times, and had remained in contact with the mother solution for one week. The material had the appearance of long hollow needles about 1/2" long.

"Eastman Kodak nitroguanidine crystals": nitroguanidine obtained from a bottle of Eastman Kodak White Label nitroguanidine.

"pressed nitroguanidine crystals": nitroguanidine that was pressed to a pellet under vacuum at a pressure of 48,000 lbs./in². This pellet was quite hard and had a density of 1.68 grams/cm³.

"ground nitroguanidine crystals with catalyst": nitroguanidine that had been ground together with 1.92% Co₂O₃ and .08% Pd by weight. This material was gray in color, but in texture similar to "ground nitroguanidine crystals".

"ground crystals from needle-like nitroguanidine crystals": needle-like nitroguanidine crystals that had been ground for two hours in a Fisher Motor-Driven Mortar Grinder.

RESULTS OF THERMAL DECOMPOSITION OF NITROGUANIDINE

1. Solid Products of Thermal Decomposition

The thermal decomposition of nitroguanidine resulted in four separate products:

1. A solid residue brownish gray in color depending on the temperature heated.
2. A white sublimate that formed at the mouth of the furnace at the junction of the hot and cold portion of the sample tube.
3. A small white sublimate in the liquid nitrogen trap.
4. Gaseous products.

The residue was examined in the infrared, but little information was obtained because of the amorphous nature of the product.

An examination of the spectrum of the sublimate, product no. 2, Figure 4, indicated the presence of nitroguanidine, dicyandiamide, and melamine. The latter two compounds are the dimer and trimer of cyanamide respectively. The infrared spectrum of pure samples of nitroguanidine, dicyandiamide, and melamine are given in Figures 4, 5, and 6. Figure 4, the spectrum of the sublimate with that of pure melamine superimposed, showed that melamine accounted for all of the infrared absorption of the sublimate with the exception of absorptions at 4.25_μ, 7.8_μ, 8.05_μ and small absorptions at 10.8_μ and 12.85_μ. The double

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absorption at 4.25μ was assigned to dicyandiamide and is in a region very characteristic of a C-N absorption (c). The absorption at 7.8μ was attributed to nitroguanidine, which has its strongest absorption in this region, due probably to the nitro group (c). Nitroguanidine has a strong absorption also at 12.8μ . Dicyandiamide has an absorption at about 8μ and another at 10.75μ from Figure 5. Thus all the differences in the spectrums of the sublimate and melamine, Figure 4, were attributed to nitroguanidine and dicyandiamide. It should be noted that the weak absorptions of the latter compounds in the sublimate seem to have shifted the peak heights to slightly longer wavelengths.

Davis and Abrams (a) have previously reported the sublimate as consisting, for the most part, of nitroguanidine and melamine.

2. Gaseous Products of Thermal Decomposition

a. Nature of Gaseous Products

Thermal decompositions of nitroguanidine were run from 160°C to 500°C , and in all cases, the gaseous products, as identified by infrared spectra, consisted of the following four gases: nitrous oxide, ammonia, water vapor, and carbon dioxide. No gases were evolved that could not be condensed in a liquid nitrogen cold trap. Tables I, II, and III give the analytical results of the thermal decomposition of nitroguanidine at 200°C , 240°C and 300°C .

b. Evolution of Nitrous Oxide

It seems quite clear from the thermal decomposition at 240°C , the so-called "melting point" of nitroguanidine, Table II, that for every mole of nitroguanidine that decomposes, one mole of nitrous oxide is evolved. We can assume that the difference between the percentage of nitroguanidine that decomposes at 240°C , as indicated by nitrous oxide, 95%, and complete decomposition, 100%, is due to sublimation of the nitroguanidine. Davis and Abrams (a) using a slightly different experimental set-up, found that 8.1% of the original starting material, nitroguanidine, was found in the sublimate and residue at $233 - 237^{\circ}\text{C}$. This latter value seems to be in good agreement with our results.

At a temperature of 300°C , Table III, only 73.4% of the nitroguanidine decomposes, according to the nitrous oxide evolved. This can be attributed to increased sublimation caused by the higher temperature and faster rate of heating of the nitroguanidine. It thus was deemed possible to calculate the degree of decomposition of nitroguanidine from the amount of nitrous oxide evolved.

c. Oxygen-Bearing Decomposition Products

The percentage of oxygen recovered in the gaseous products, based on the amount of oxygen available from nitroguanidine that actually decomposes (not including sublimed nitroguanidine), is of the order of 91% oxygen (O) for the three temperatures measured. Davis and Abrams (a), analyzing the residue, found 10.5% oxygen in the form of ammeline and ammelide present. Their value is in good agreement with our value of approximately 9% oxygen by difference. The scheme of decomposition proposed by Davis and Abrams (a), is given

Table I

Decomposition of Nitroguanidine at 200°C

Run A: Nitroguanidine heated for 20 minutes at 200°C + 1°C
Run B: Nitroguanidine heated for 30 minutes at 200°C + 1°C
Run C: Nitroguanidine heated for 90 minutes at 200°C + 1°C

	Run A		Run B		Run C	
	Moles x 10 ⁴	Ratio N ₂ O/NH ₃	Moles x 10 ⁴	Ratio N ₂ O/NH ₃	Moles x 10 ⁴	Ratio N ₂ O/NH ₃
H ₂ O	7.99	2.96	12.18	3.0	13.5	3.3
NH ₃	2.7		4.06		4.08	
H ₂ O	5.27		8.3		9.62	
CO ₂	.73		.86		.68	
Nitroguanidine Starting Material	58.3		42.3		19.6	
<hr/>						
	Run A		Run B		Run C	
% Nitroguanidine Decomposed Based on H ₂ O	13.7		28.8		68.8	
Wt. % of Total Decomposed Material Appearing As Gaseous Products	62.9		62.4		59	
<hr/>						
<u>Oxygen Balance</u>						
	Run A		Run B		Run C	
	mg O		mg O		mg O	
H ₂ O	12.78		19.45		21.6	
H ₂ O	8.43		13.3		15.33	
CO ₂	2.33		2.76		2.18	
Total	23.54		35.51		39.1	
Available Oxygen from Decomposed Nitroguanidine	25.56		38.90		43.2	
% O Recovered	92.1		91.3		90.5	

Table II

Decomposition of Nitroguanidine at 240 - 242°C
Heated for 26 Minutes

	Run A Moles x 10 ⁴	Ratio N ₂ O/NH ₃	Run B Moles x 10 ⁴	Ratio N ₂ O/NH ₃	Run C Moles x 10 ⁴	Ratio N ₂ O/NH ₃
N ₂ O	12.25		12.32		12.22	
NH ₃	3.96	3.1	4.29	2.9	4.1	3.0
H ₂ O	8.82		9.21		8.04	
CO ₂	.91		.84		.84	
Nitroguanidine Starting Material	12.8		12.8		12.8	
1						
	Run A		Run B		Run C	
% Nitroguanidine Decomposed Based on N ₂ O	95.7		96.4		95.5	
Wt. % of Total Decomposed Mater- ial Appearing as Gaseous Products	63.0		63.7		62	
Oxygen Balance						
	Run A mg O		Run B mg O		Run C mg O	
N ₂ O	19.55		19.7		19.52	
H ₂ O	44.13		14.75		12.88	
CO ₂	2.91		2.69		2.69	
Total	36.6		37.14		35.1	
Available Oxygen from Decomposed Nitroguanidine	39.2		39.4		39.0	
% Oxygen Recovered	93.4		94.3		89.9	

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Table III

Decomposition of Nitroguanidine at 300 - 302°C
Heated for 26 Minutes

	<u>Moles x 10⁴</u>	<u>Ratio N₂O/NH₃</u>
N ₂ O	9.41	2.83
NH ₃	3.32	
H ₂ O	6.41	
CO ₂	9.6	
Nitroguanidine Starting Material	12.82	
<hr/>		
% Nitroguanidine Decomposed Based on N ₂ O	73.4	
Wt. % of Gaseous Products to Total Decomposed Material	64.1	

	<u>Oxygen Balance</u>
	<u>Mg O</u>
N ₂ O	15.05
H ₂ O	10.25
CO ₂	<u>3.06</u>
Total	28.36
Available Oxygen From Decomposed Nitroguanidine	31.1
% O Recovered	94.1

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in Figure 7. Davis and Abrams (a) did not find any oxygen-bearing compounds in the sublimate other than sublimed nitroguanidine. It can therefore be stated that the oxygen-bearing products from the decomposition of nitroguanidine are nitrous oxide, carbon dioxide, water, ammeline, and ammelide. The amounts of cyanic acid, cyanuric acid, and urea formed must be negligible.

d. Evolution of Ammonia and Water

Tables I, II, and III indicate that the amount of ammonia and water formed in the decomposition equals the amount of nitrous oxide evolved. This fact is in good agreement with the scheme of Davis and Abrams (a), Figure 7. According to the scheme of Davis and Abrams (a), ammonia is evolved in the following three ways: directly from the portion of the reaction that precedes by step II, from the hydrolysis of cyanic acid to carbon dioxide, from the deammonolysis of melamine to melam, melam, and mellon. The total ammonia and carbon dioxide evolved is known. The ammonia evolved in the formation of melam, melam, and mellon can be calculated from the data of Davis and Abrams. Therefore, the ammonia evolved as a direct result of nitroguanidine decomposing by step II can be calculated. From the latter value, the percentage of the thermal decomposition proceeding by step II, according to Davis and Abrams (a), is calculated as approximately $23\% + 2\%$.

An alternate method for determining the percentage of the reaction proceeding by step II is to measure the total amount of products that are present as a result of the formation of cyanic acid. These products are carbon dioxide, ammeline, and ammelide. Using the values of Davis and Abrams (a) for ammeline and ammelide, and the measured value of carbon dioxide, the percentage of reaction proceeding by step II is 26%. The latter value is not nearly as reliable as the former one, because it neglects any hydrolysis of cyanamide to cyanic acid in the formation of ammeline and ammelide.

e. The Ratio of Nitrous Oxide to Ammonia

The ratio of nitrous oxide to ammonia is quite important in the ignition of nitroguanidine as a propellant and seems to decrease with increasing temperature. The ratio is about 3:1 at 200°C and 2.8:1 at 300°C.

Figure 9 shows the spectrum of the gaseous products of a sample of nitroguanidine decomposed at 170°C. Figure 10 is the spectrum of the gaseous products from the solid residue of a 240°C decomposition that was reheated to 500°C. These spectra clearly show that at higher temperatures the ratio of nitrous oxide to ammonia evolved is lower. This is, to some extent, due to the deammonolysis of melam and melam to mellon. The reheated residue was colored a bright yellow, which is very characteristic of mellon.

DISCUSSION OF RESULTS

1. Mechanism of Thermal Decomposition

We have shown that, according to the scheme of Davis and Abrams (a) for the decomposition of nitroguanidine, approximately 77% of the nitroguanidine at 240°C decomposes by step I. An alternative proposal that explains the observed facts is that all of the nitroguanidine decomposes by step I. The

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evolution of ammonia then is a result of the hydrolysis of cyanamide and its polymers. This scheme is portrayed in Figure 8. The scheme can be tested by calculating from the amount of ammeline, ammelide, and carbon dioxide present, how much ammonia would be evolved due to their formation by hydrolysis. The percentage of ammonia evolved of the total decomposed nitroguanidine is thus calculated as $38\% + 2\%$. The actual percentage of ammonia evolved was 33.5%.

The latter alternative scheme, and Davis and Abrams scheme (a), are in harmony with all the experimental facts as discussed in paragraphs 2 a, b, c and d. From the data given, it is not possible to distinguish between the two schemes as to which is the correct one. However, we have shown that our experimental data is in good agreement with both of them, and that at least 77% of the nitroguanidine decomposes to nitramide and cyanamide.

2. Application to Burning of Nitroguanidine Propellants

The thermal decomposition of nitroguanidine proceeds in the following manner:

Solid \rightarrow Gaseous + Solid Products

When nitroguanidine burns as a propellant, the stepwise process probably consists of an endothermic thermal decomposition to gaseous products, which in turn combine in an exothermic reaction. From the nature of the gases that are evolved, the exothermic reaction is that of the reaction between ammonia and nitrous oxide. At the surface of a burning nitroguanidine propellant, nitrous oxide and ammonia are evolved in the ratio from our thermal decomposition studies, of 3:1. The solid products, which are probably dispersed in a higher temperature zone between the surface and the flame zone, decompose or are hydrolyzed, to enrich the nitrous oxide - ammonia mixture to a limiting value of about 1:1. The fact that the nitrous oxide ammonia ratio is high near the surface, higher in fact than the stoichiometrical equation allows, may be of significance in explaining the irregular burning of nitroguanidine, its difficulty of ignition, and the high pressure exponent in the burning rate of nitroguanidine.

RESULTS OF KINETICS OF THERMAL DECOMPOSITION

1. The Kinetic Rate Equation

The rate at which nitroguanidine decomposes has been studied over a temperature range of 181°C to 200°C. The extent of decomposition has been determined from the amount of nitrous oxide evolved, which has been shown to be a measure of decomposed nitroguanidine. The kinetic runs were carried out under a pressure of less than 1 mm. throughout the experiment -- the gaseous products being continually withdrawn. This procedure minimized the possibility of interaction between gaseous products and the undecomposed nitroguanidine.

The rate law which seems to fit the data over a good portion of the decomposition is the following:

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$$dN/dt = -k N_0 \left[1 - c \left(\frac{N_0 - N}{N_0} \right) \right] \quad (1)$$

N = the amount of undecomposed nitroguanidine

N_0 = the initial amount of nitroguanidine present

k = a zero order rate constant

c = a constant that depends on the relative efficiency of the inhibiting factors of the reaction

t = time

Equation (1) may be derived in the following way. It is assumed that only those molecules that are at a surface or are exposed by a newly created surface can decompose. The rate of decomposition will be proportional to the number of B active sites on the surface. These active sites are assumed to be situated at lattice imperfections in the crystal and are mostly on the surface. They will be produced in the neighborhood of decomposing molecules on the surface of the crystal, due to strains set up during the decomposition, and also due to the exposure of new crystal surface. B will depend on the total surface area of the crystals which is designated S at any time t.

$$dN/dt = -k_1 S \quad (2)$$

Experimentally it is found that the reaction is inhibited as the decomposition proceeds and does not follow equation 2; consequently another factor must be introduced which allows for the decrease in the number of B active sites with increasing decomposition. The equation below expresses this fact:

$$dN/dt = -k_1 B = -k_1 S \left[1 - c \left(\frac{N_0 - N}{N_0} \right) \right] \quad (3)$$

The actual physical process of inhibition may be due to the fact that solid decomposition products remain on the surface of the decomposing material and prevent the creation of new surface. The strength of the inhibition is indicated by the value of c.

If B depends on the total surface area, then it would be expected that the rate would depend on N to some power. For instance in the case of a cubic crystal: $S = k_1 N^{2/3}$. Nitroguanidine, however, crystallizes from water as long, thin, hollow needles. See Figure 11. In this case, the geometry is such that the surface area would not decrease appreciably in time or with increasing decomposition. This is especially true if reaction takes place on both inner and outer surfaces of the hollow needles. Therefore, S for nitroguanidine is proportional to N_0 for the whole decomposition, and consequently equation (3) becomes

$$dN/dt = -k N_0 \left[1 - c \left(\frac{N_0 - N}{N_0} \right) \right] \quad (1)$$

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2. Kinetic Characteristics of Decomposition

The thermal decomposition of nitroguanidine after approximately fifteen to twenty percent decomposition seems to follow the zero order rate law of equation (1). A curve of percentage decomposition versus time, plotted in accordance with a first order rate law, indicated the decomposition does not obey first order kinetics over any part of the reaction.

Studies on initial rates were not thoroughly investigated because of a time lag due to the heating up of the solid sample from room temperature. One run was attempted with "ground nitroguanidine crystals" in which points were obtained for low values of time and percentage decomposition. The results are plotted in Figure 12. The plot clearly shows that the initial decomposition rate seems to be zero order. Moreover, no initial acceleratory region seems to be in evidence as described by Prout and Tompkins (e,f) in the thermal decomposition of permanganate salts.

The percentage decomposition of nitroguanidine for various times does not vary according to the initial size of the sample as determined by experiment. This fact is generally true of first order reactions, but can be true for a zero order reaction that occurs on a surface, the size of which depends on the initial concentration of the reactant.

3. Evaluation of Rate Constants

The value of k and c were obtained by first plotting an $(N_0 - N)/N_0$ vs t curve. Values of $-1/N_0 dN/dt$ obtained from this curve were plotted against $(N_0 - N)/N_0$. If equation (1) holds, the latter curve should be a straight line whose slope is $-kc$ and whose intercept is $1/c$. The values of k and c for various species of nitroguanidine are given in Table IV. Figures 13 - 20 are plots of $(N_0 - N)/N_0$ vs t curves and $-1/N_0 dN/dt$ vs. $(N_0 - N)/N_0$ curves for some of the samples listed in Table IV.

A plot of $-\log k$ vs $1/T$ is given on Figure 21 and the following rate expression is calculated:

$$k = 8.75 \times 10^{22} e^{-57,100/RT} \text{ sec.}^{-1}$$

$$R = 1.99 \text{ cal./mole } ^\circ K$$

$$T = ^\circ K$$

4. Rate of Decomposition for Various Species of Nitroguanidine

Table IV indicates that the "ground nitroguanidine crystals", "ground nitroguanidine crystals with catalyst", and "pressed nitroguanidine crystals" have about the same value of k at $189^\circ C$. However, the values of c differ quite markedly. Pressing the "ground nitroguanidine crystals" into a pellet form apparently did not affect the number of active sites, but did increase the inhibition. The "ground nitroguanidine crystals with catalyst" sample appeared to be very strongly inhibited. The "needle-like nitroguanidine crystals" sample gave a much higher k value than the "ground nitroguanidine crystals" sample.

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Table IV

Kinetic Data for the Decomposition of Nitroguanidine

Temperature 180°C

<u>Species</u>	<u>k(min.⁻¹)</u>	<u>c</u>
"ground nitroguanidine crystals"	.00199	3.28

Temperature 189°C

<u>Species</u>	<u>k(min.⁻¹)</u>	<u>c</u>
"ground nitroguanidine crystals"	.00447	1.83
"ground nitroguanidine crystals with catalyst"	.0048	2.73
"pressed nitroguanidine crystals"	.0045	2.31
"ground crystals from needle-like nitroguanidine"	.00528	2.32
"Eastman Kodak nitroguanidine crystals"	.00602	1.68
"needle-like nitroguanidine crystals"	.011	1.63

Temperature 195.4°C

<u>Species</u>	<u>k(min.⁻¹)</u>	<u>c</u>
"ground nitroguanidine crystals"	.0133	1.6

Temperature 200°C

<u>Species</u>	<u>k(min.⁻¹)</u>	<u>c</u>
"ground nitroguanidine crystals"	.0266	1.40
"ground nitroguanidine crystals"	.0223	1.27
"ground nitroguanidine crystals"	.0288	1.30

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This might be due to the fact that these large crystals had more active spots than the smaller more perfect crystals. It is also likely that occluded mother liquor in the long "needle-like crystals" caused the large increase in the value of k . This is suggested by the fact that grinding the "needle-like crystals", which might have allowed the trapped water to escape, reduced the value of k to a slightly higher value than the "ground nitroguanidine crystals" value of k . The fact that the "Eastman Kodak crystals" showed the worst deviation from equation (1) indicates that they probably consisted of a mixture of different species of nitroguanidine.

The constant c decreases with increasing temperature, perhaps because of increased decomposition or sublimation of solid products that cause inhibition in the rate. The exact nature of the inhibiting factors have not been experimentally determined. One, or a number of the solid products, could have caused inhibition. The possibility of one of the gaseous products causing inhibition by being absorbed on the surface cannot be discounted, even though the decomposition took place under low pressure throughout.

Several photomicrographs of "ground nitroguanidine crystals" for various percentage decompositions are given in Figures 22 and 23. These photographs indicate the larger crystals decompose faster than the smaller ones. Moreover, by 15% decomposition, it appears that the outer surface of the nitroguanidine crystal is almost completely covered with decomposing material. This is in accord with our observation that equation (1) holds for decompositions above 15%.

SUMMARY

The gaseous products of the thermal decomposition of nitroguanidine from 160°C to 500°C are nitrous oxide, ammonia, water vapor, and carbon dioxide. At 240°C, 90% of the oxygen present in nitroguanidine appears in the gaseous products. The ratio of nitrous oxide to ammonia evolved at 240°C is 3:1. The primary exothermic reaction in the burning of nitroguanidine is the reaction between nitrous oxide and ammonia. The mechanism of the thermal decomposition involves the initial formation of nitramide and cyanamide to the extent of at least 77%. The suggestion has been proposed that the evolution of ammonia is due to the hydrolysis of cyanamide and its polymers.

Nitroguanidine decomposes, after approximately 15% decomposition, according to the rate law given below:

$$dN/dt = -k N_0 \left[1 - c \left(\frac{N_0 - N}{N_0} \right) \right]$$

where

$$k = 8.75 \times 10^{22} e^{-57,100/RT} \text{ sec.}^{-1}$$

The thermal decomposition appears to be inhibited by solid or gaseous products.

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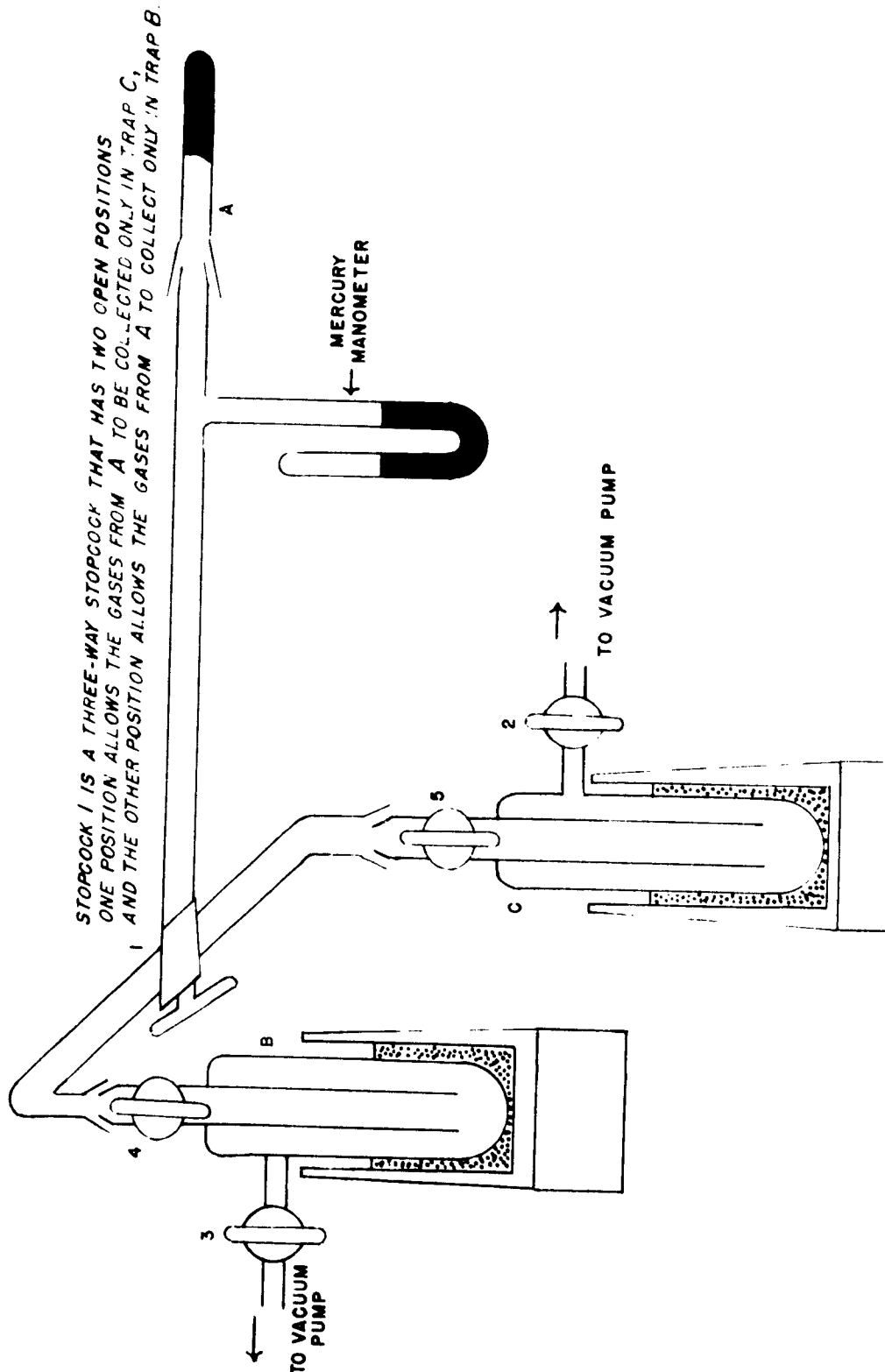


FIG. 1 APPARATUS FOR COLLECTING GASEOUS PRODUCTS OF THE THERMAL DECOMPOSITION
OF NITROGUANIDINE

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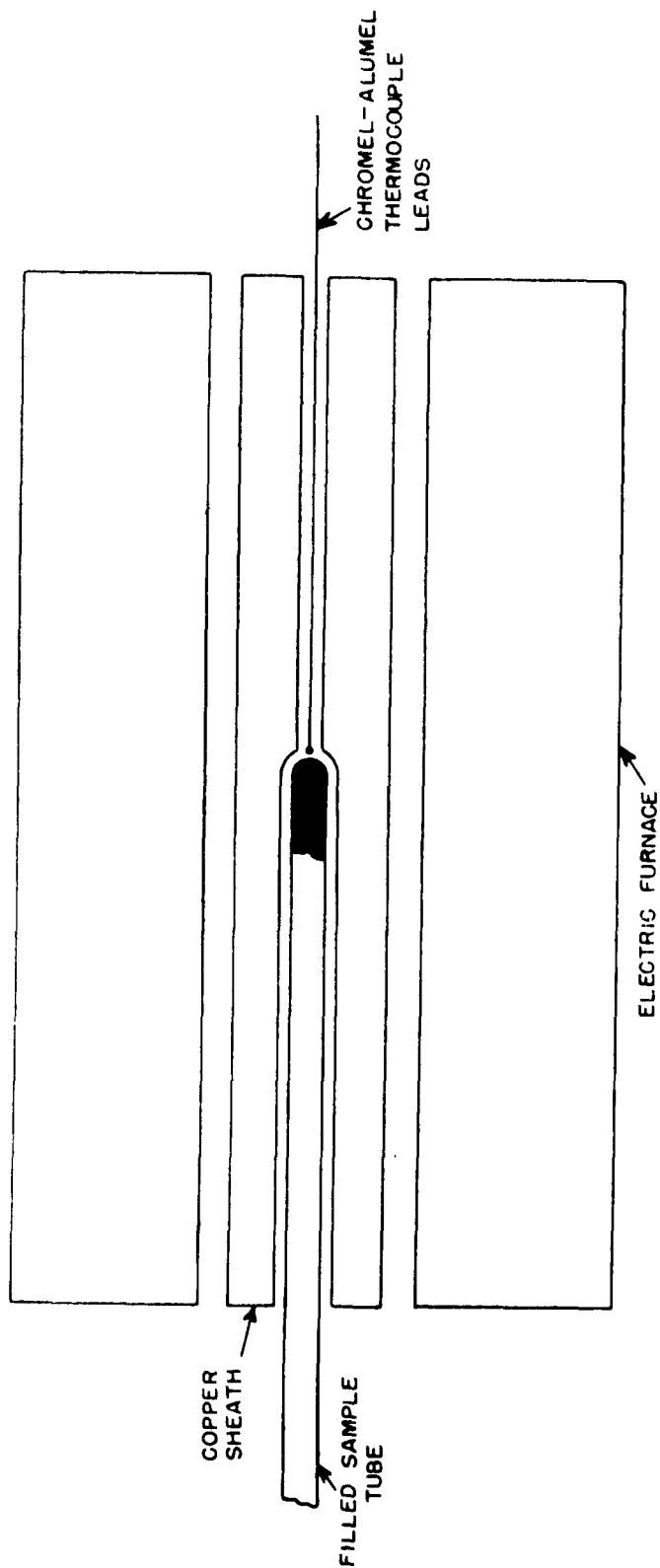


FIG. 2 CROSS SECTION OF HEATING UNIT WITH SAMPLE TUBE IN PLACE

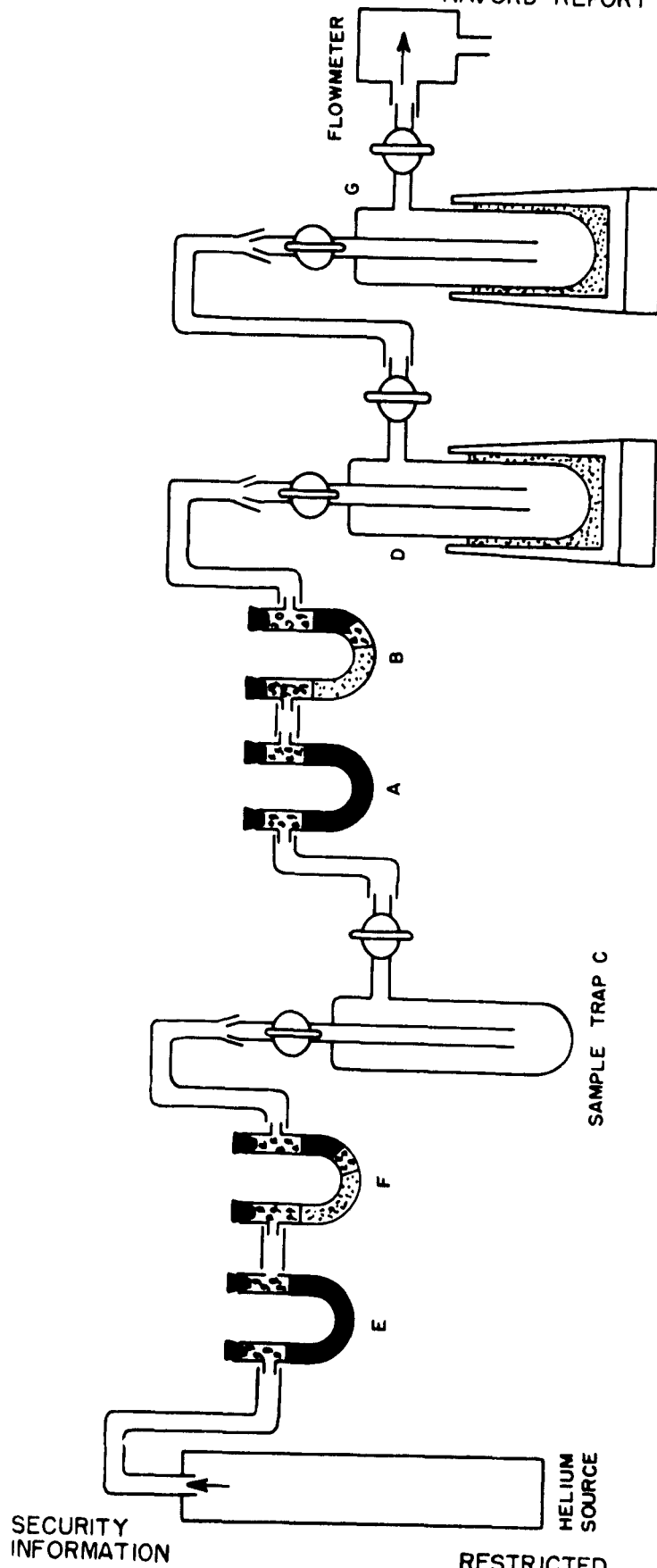
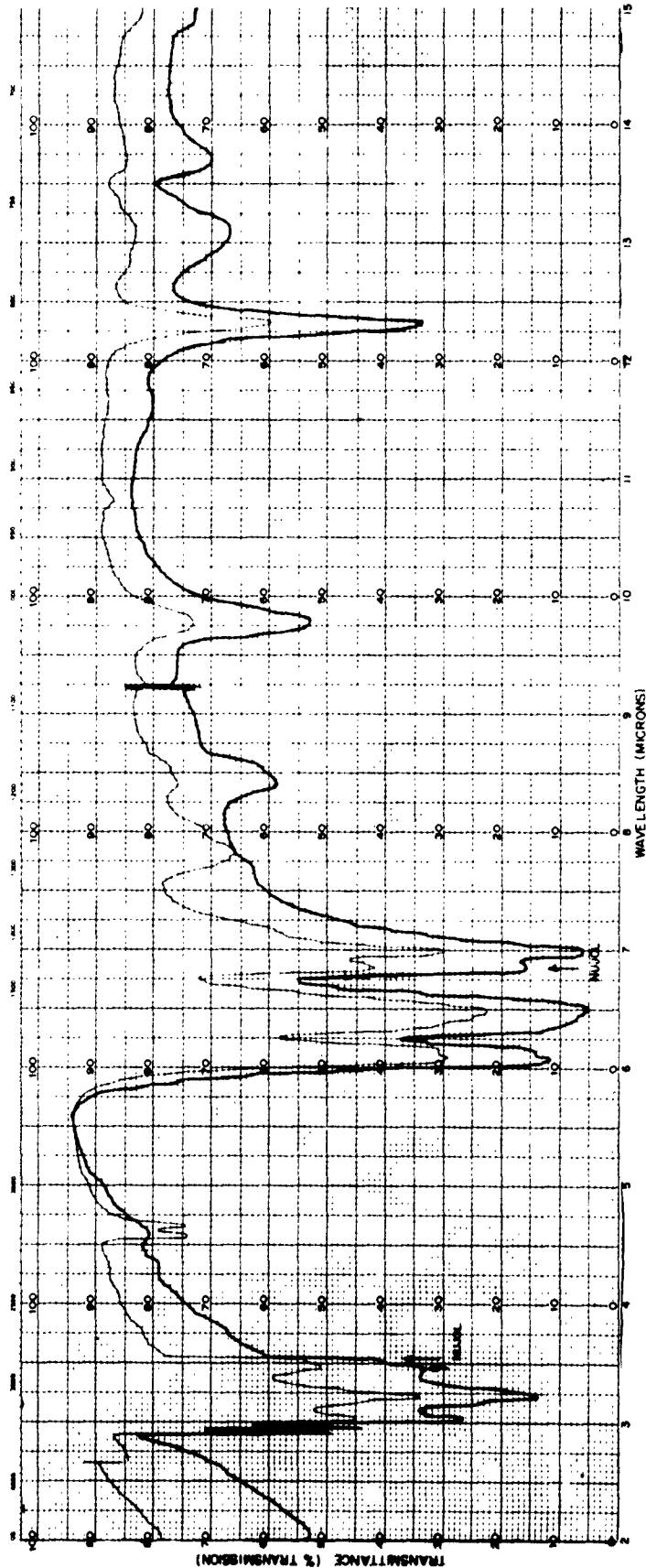


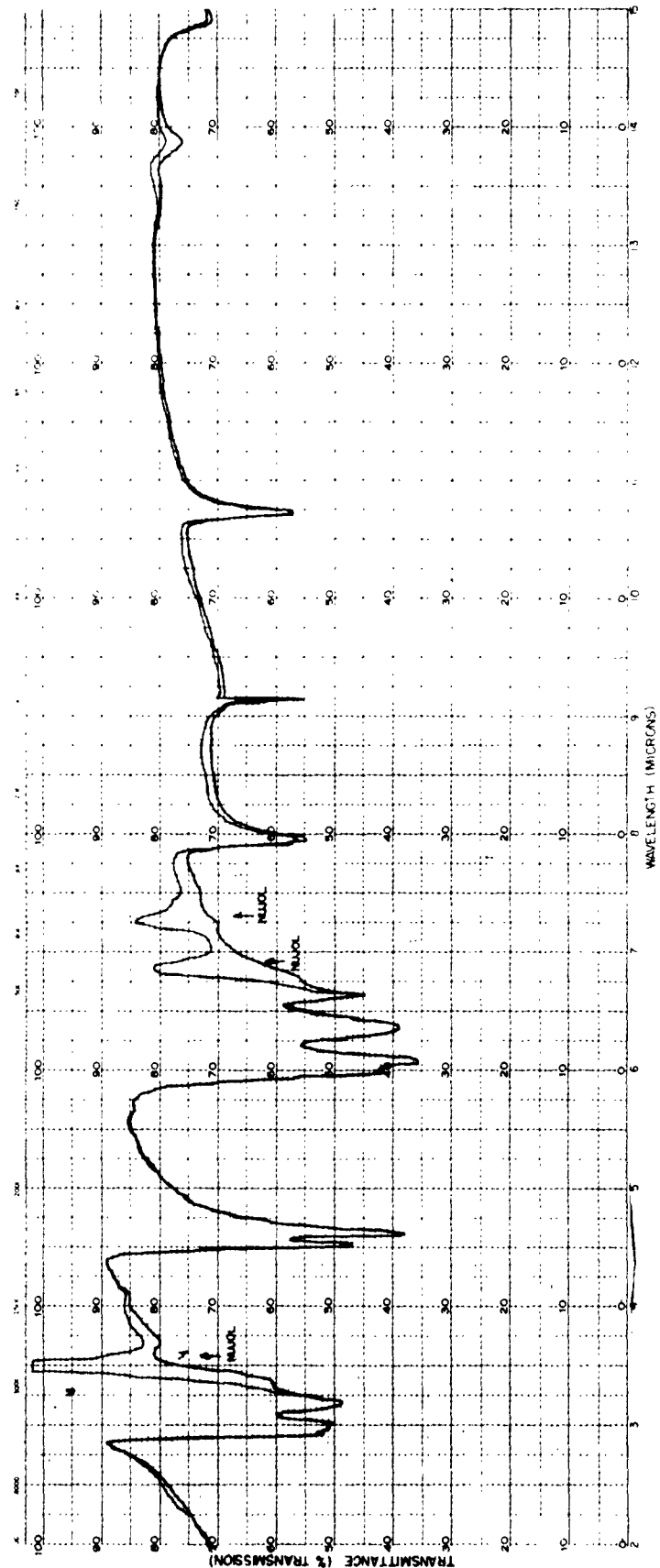
FIG. 3 ABSORPTION TRAIN FOR GASEOUS PRODUCTS OF THERMAL DECOMPOSITION

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UPPER CURVE: INFRARED SPECTRUM OF THE SUBLIMATE SUSPENDED IN NUJOL
LOWER CURVE: INFRARED SPECTRUM OF MELAMINE SUSPENDED IN NUJOL

FIG. 4 THE INFRARED SPECTRUM OF MELAMINE AND THE SUBLIMATE
OF A 240°C THERMAL DECOMPOSITION OF NITROGUANIDINE



UPPER CURVE: SHOWS MORE NUJOL PRESENT IN THE REFERENCE BEAM THAN IN THE SAMPLE BEAM
LOWER CURVE: SHOWS APPROXIMATELY THE SAME AMOUNT OF NUJOL IN THE REFERENCE AND SAMPLE PATHS

FIG. 5 THE INFRARED SPECTRUM OF DICYANDIAMIDE SUSPENDED IN NUJOL

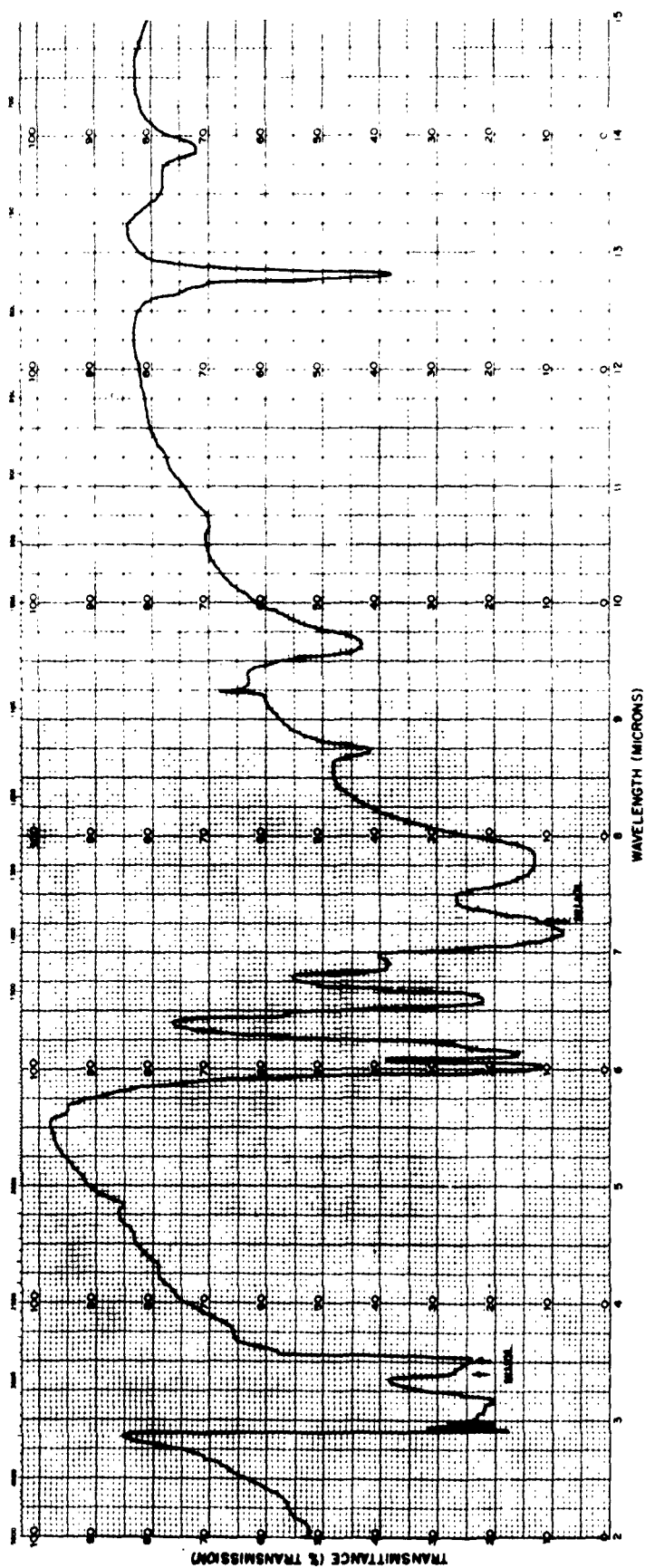


FIG. 6 THE INFRARED SPECTRUM OF GROUND NITROGUANIDINE CRYSTALS
SUSPENDED IN NUJOL

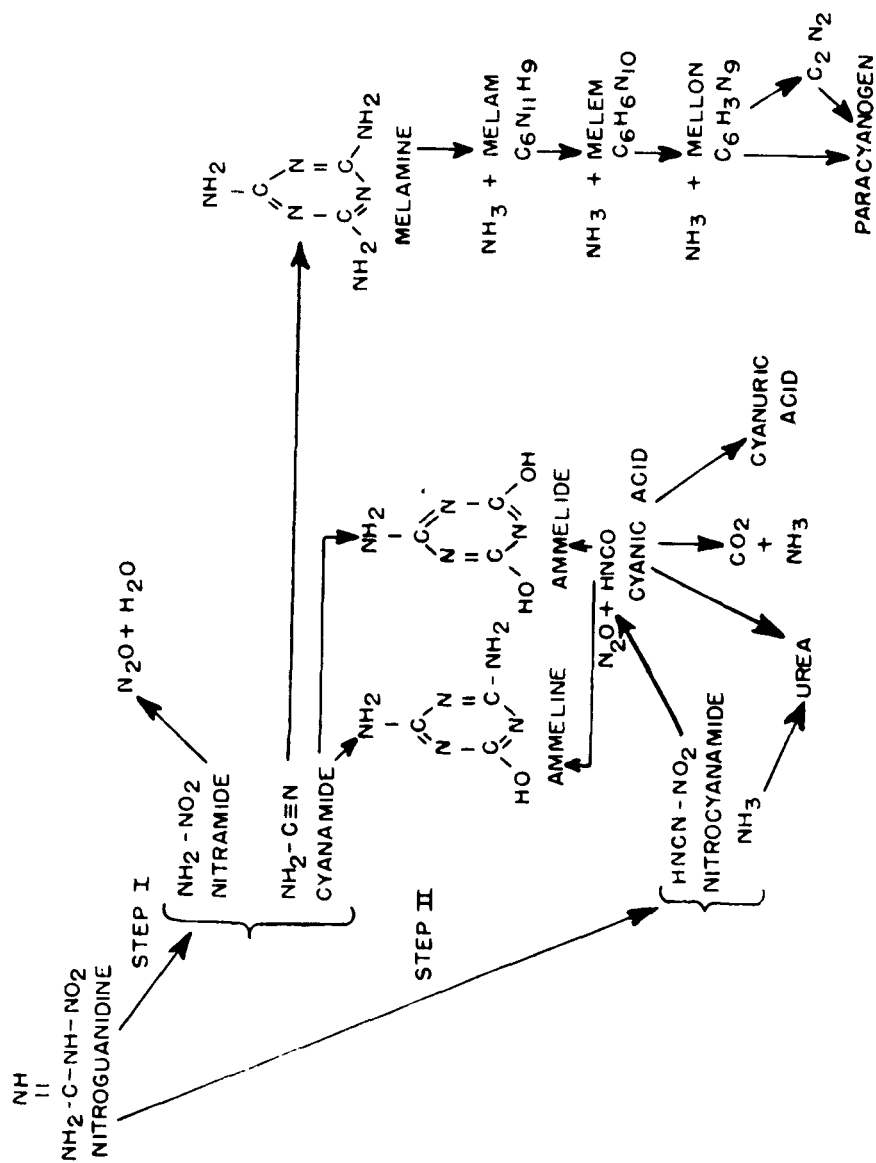


FIG. 7 THE PROPOSED SCHEME OF DAVIS AND ABRAMS FOR THE THERMAL DECOMPOSITION OF NITROGUANIDINE

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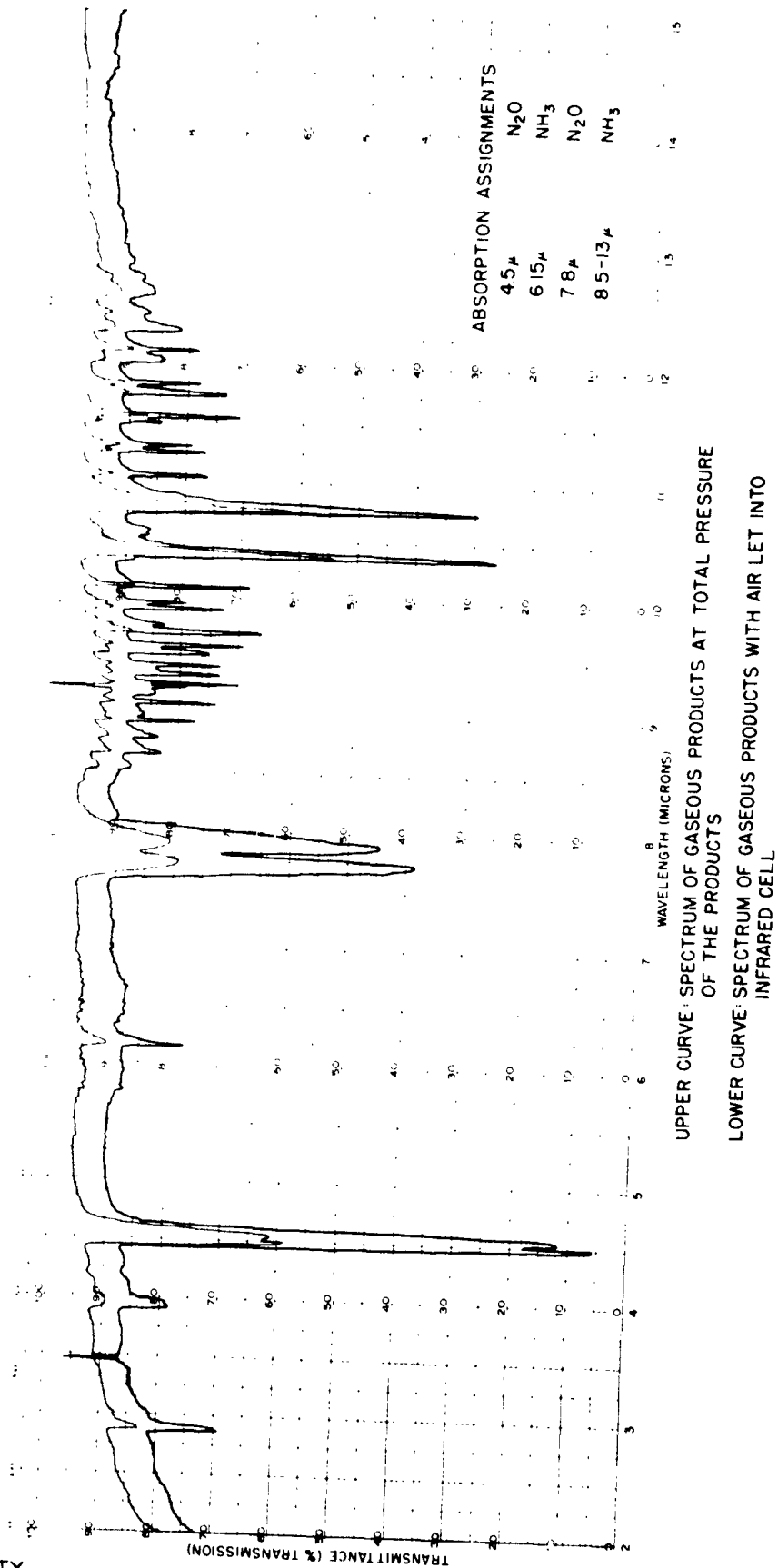
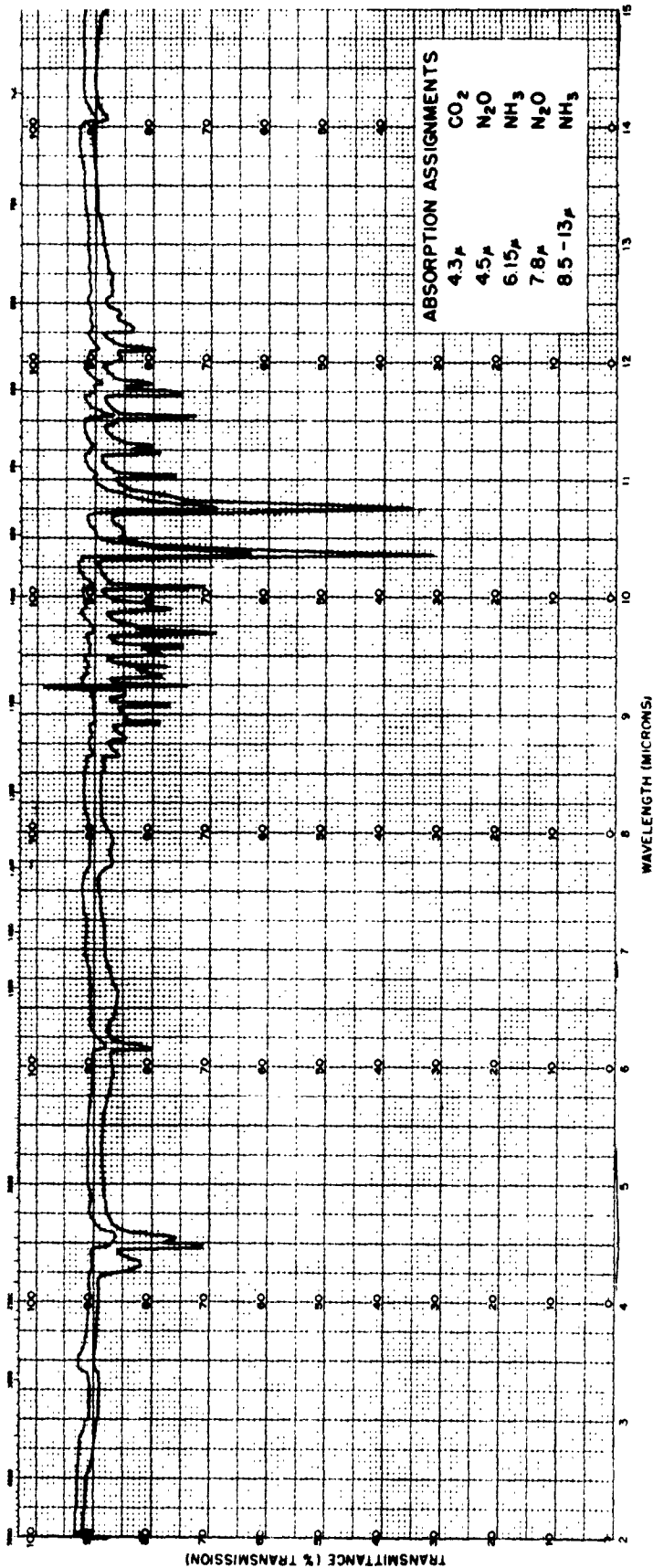


FIG. 9 THE INFRARED SPECTRUM OF THE GASEOUS PRODUCTS OF THE THERMAL DECOMPOSITION OF NITROGUANIDINE AT 170°C

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UPPER CURVE : SPECTRUM OF GASEOUS PRODUCTS AT TOTAL PRESSURE OF
THE PRODUCTS
LOWER CURVE : SPECTRUM OF GASEOUS PRODUCTS WITH AIR LET INTO
INFRARED CELL

FIG. 10 INFRARED SPECTRUM OF THE GASEOUS PRODUCTS FROM THE SOLID RESIDUE
OF A 240°C DECOMPOSITION REHEATED TO 500°C

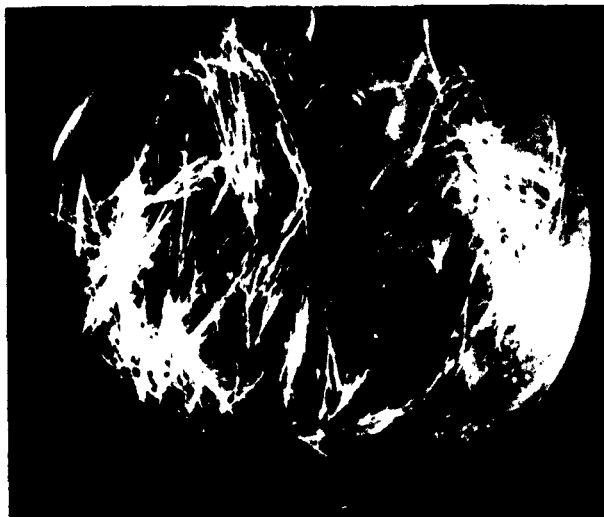


FIG. 11 "NEEDLE-LIKE NITROGUANIDINE
CRYSTALS" IN AQUEOUS SOLUTION VIEWED
FROM THE BOTTOM OF AN ERLLENMEYER FLASK

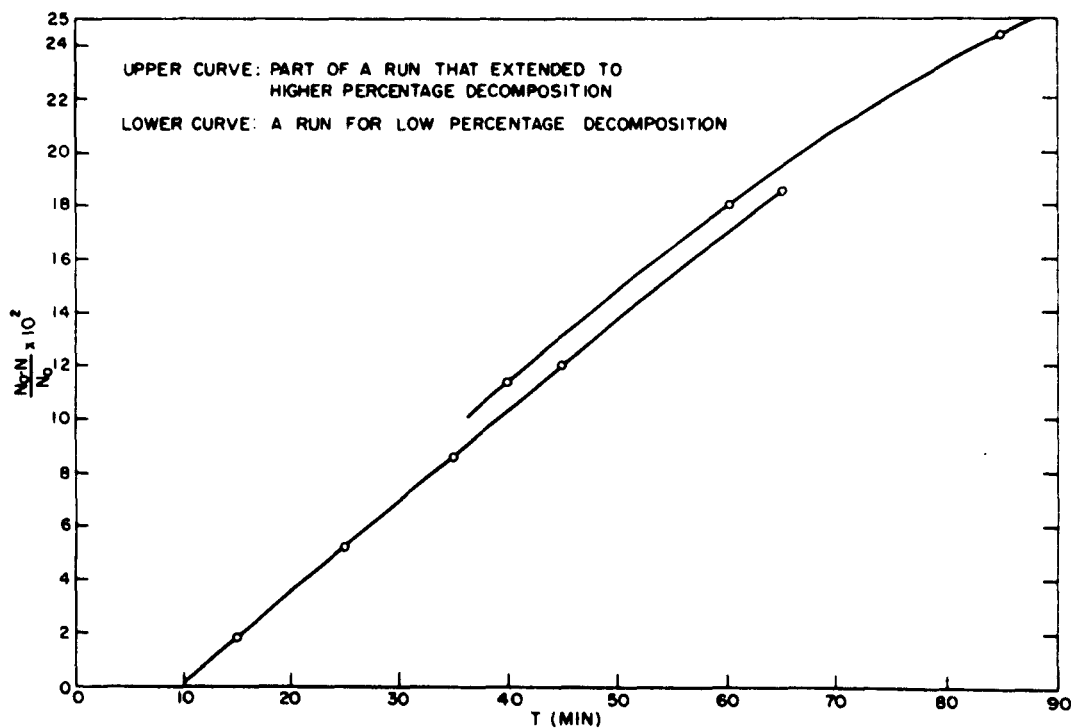
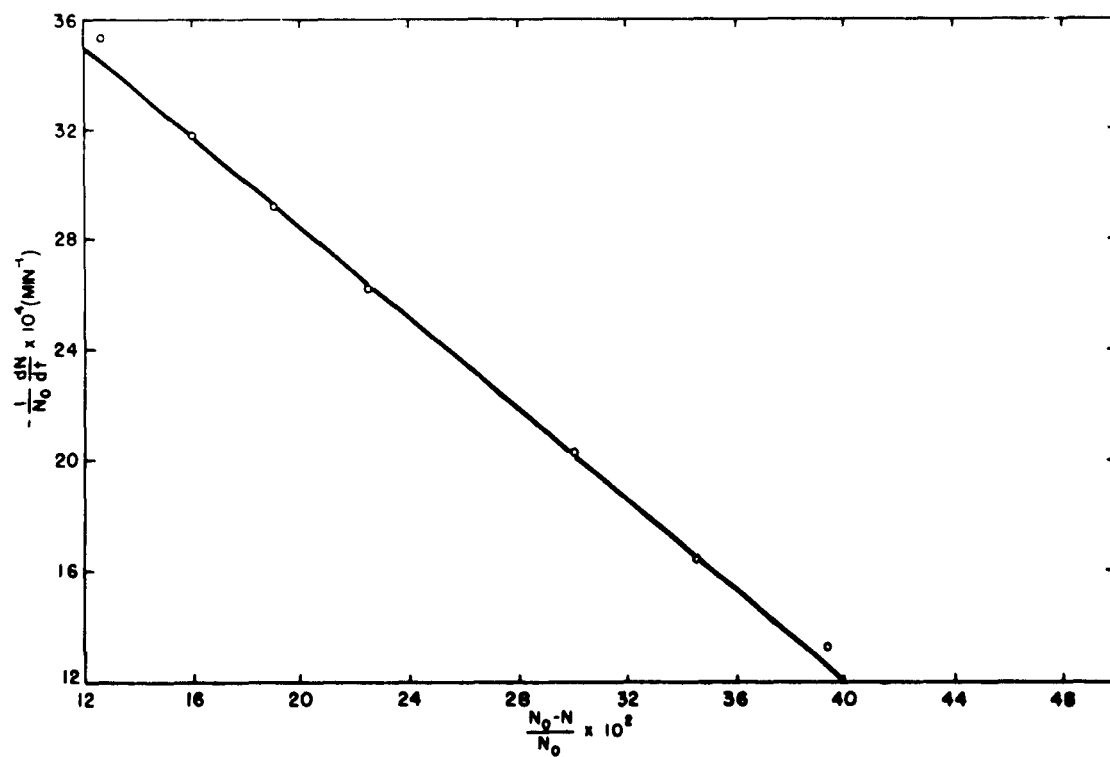
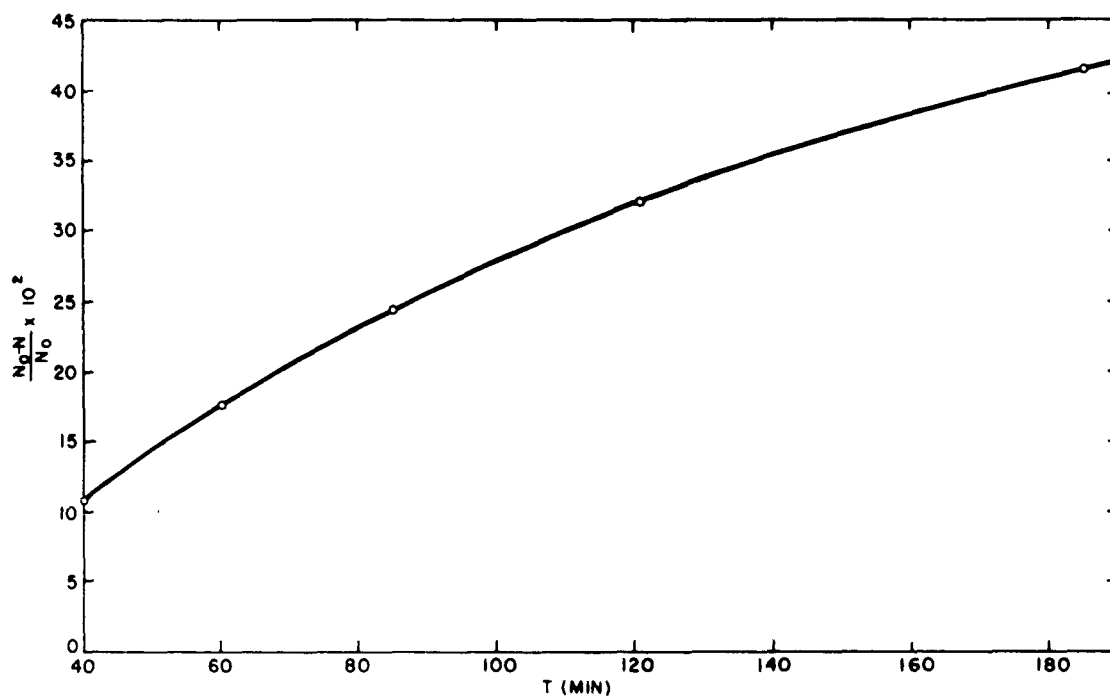


FIG. 12 THERMAL DECOMPOSITION "GROUND NITROGUANIDINE
CRYSTALS" AT 189°C FOR LOW TIMES AND PERCENTAGE
DECOMPOSITION

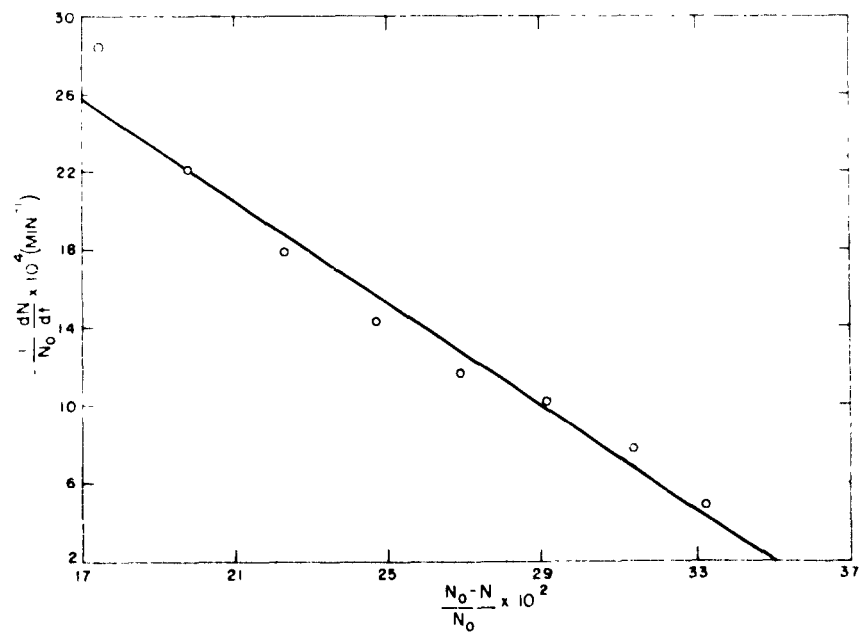
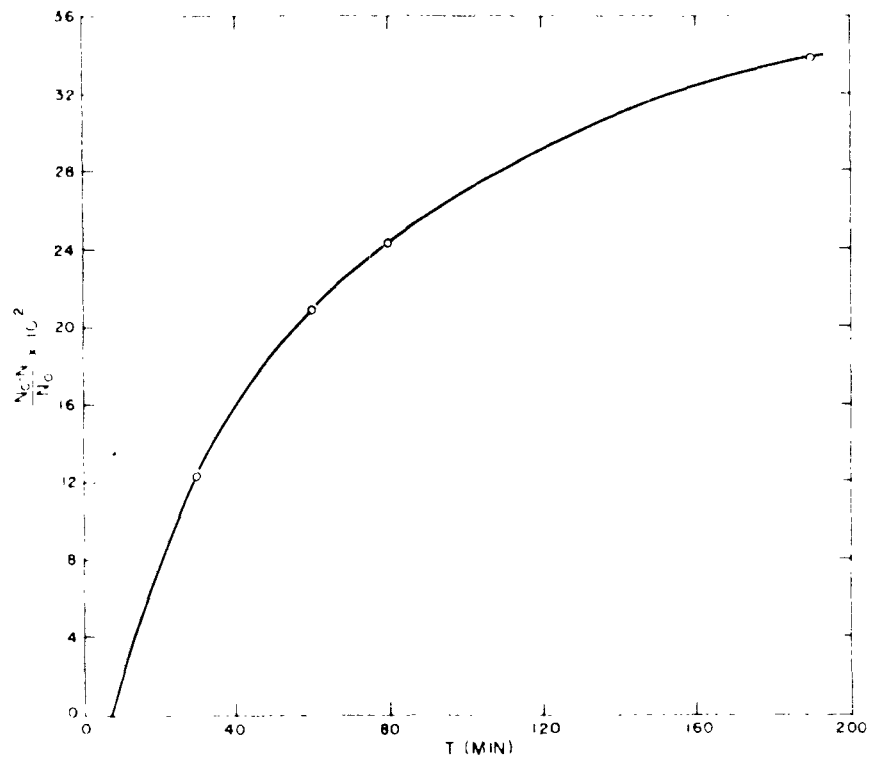
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FIG. 13 THERMAL DECOMPOSITION OF "GROUND
NITROGUANIDINE CRYSTALS" AT 189° C



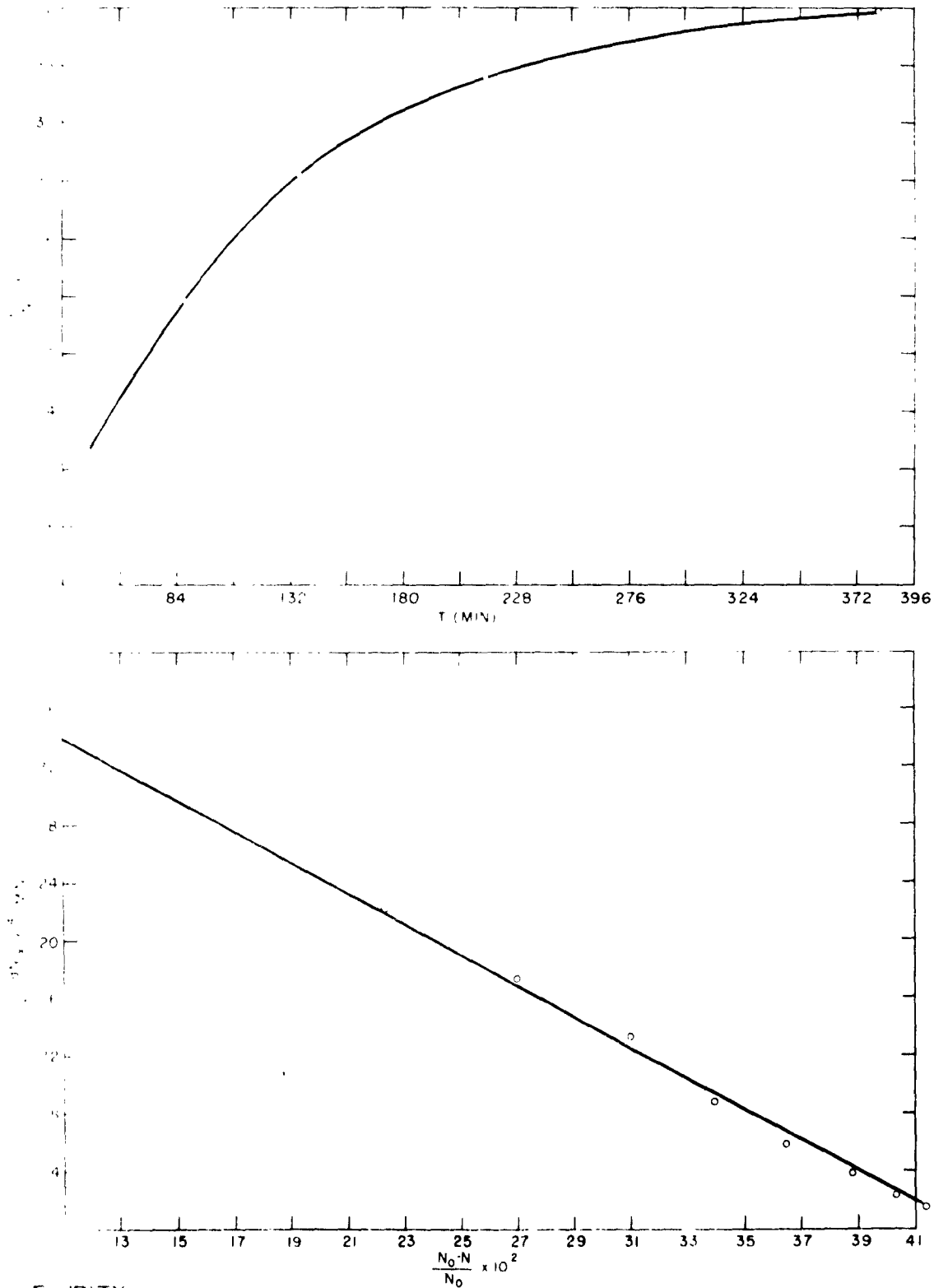
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FIG. 14 THERMAL DECOMPOSITION OF "GROUND
NITROGUANIDINE CRYSTALS WITH CATYLYST" AT 189 °C



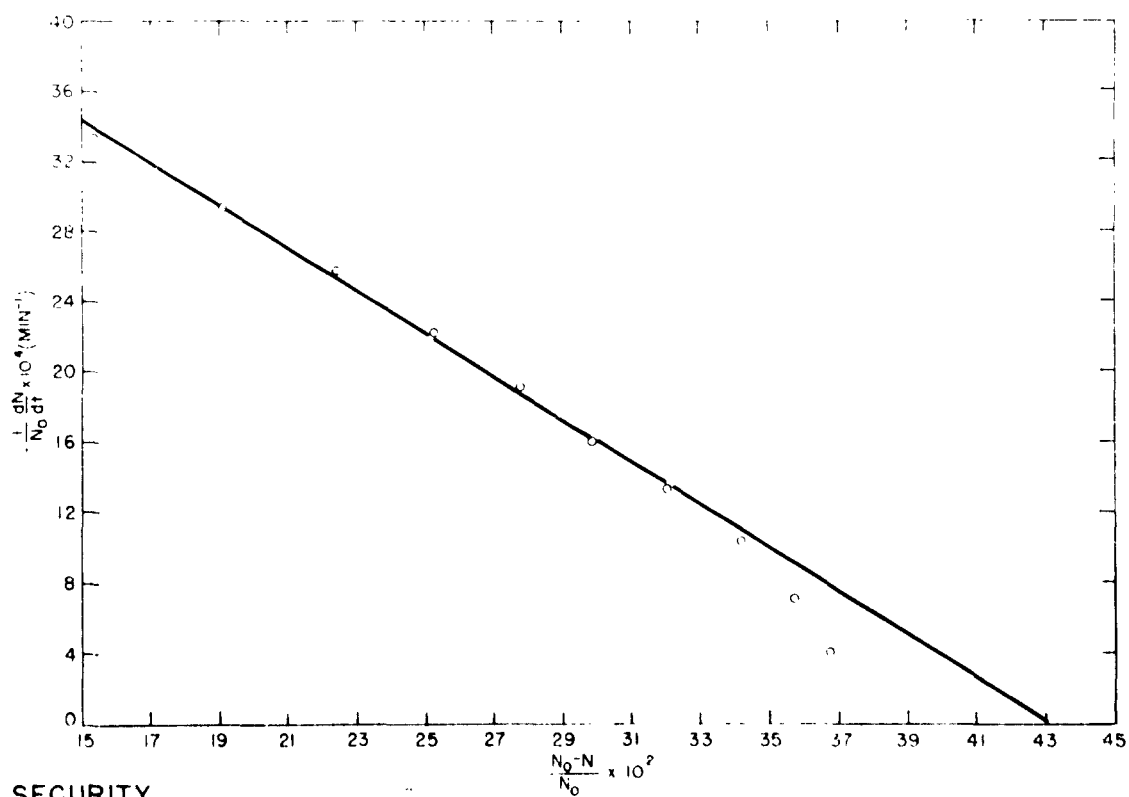
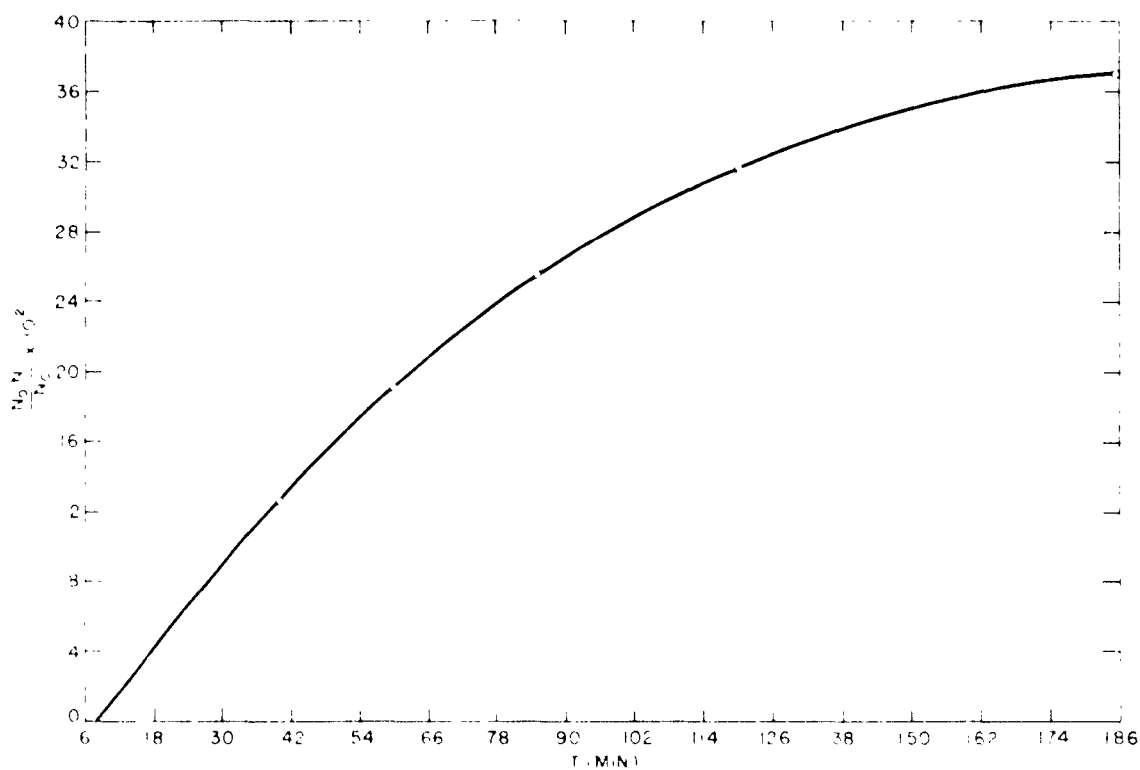
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FIG 15 THERMAL DECOMPOSITION OF "PRESSED
NITROGUANIDINE CRYSTALS" AT 189° C



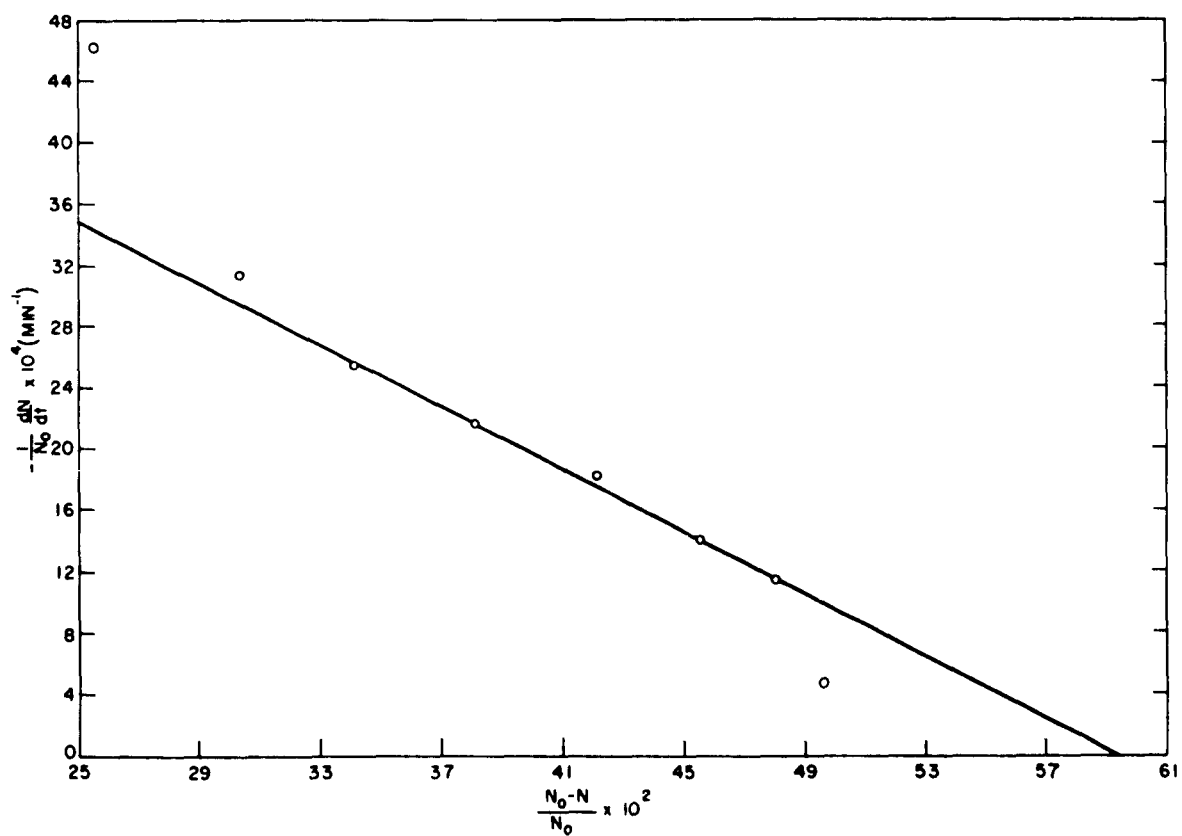
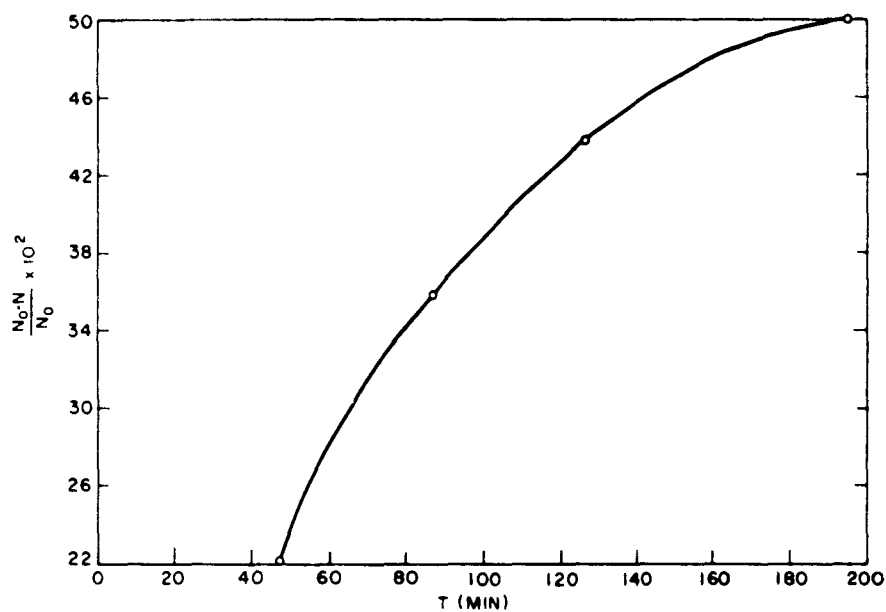
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FIG 16 THERMAL DECOMPOSITION OF "GROUND CRYSTALS
FROM NEEDLE-LIKE NITROGUANIDINE" AT 189°C



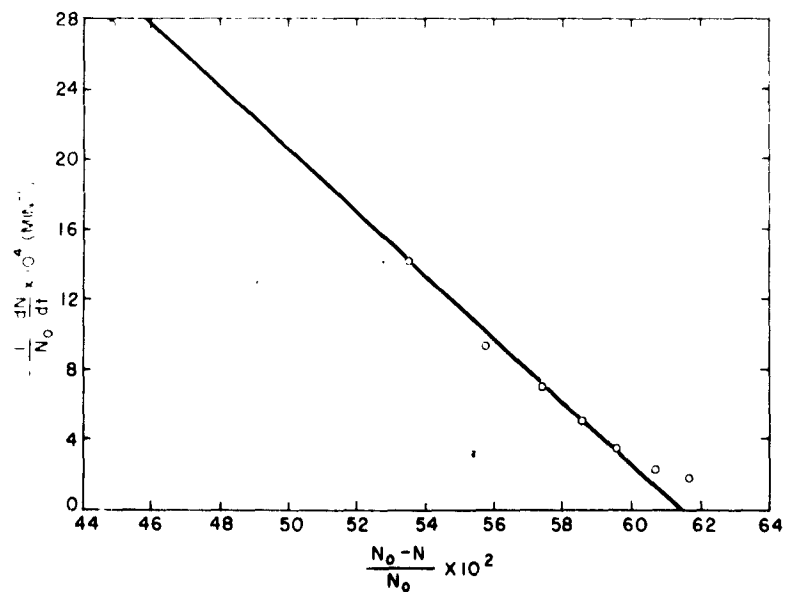
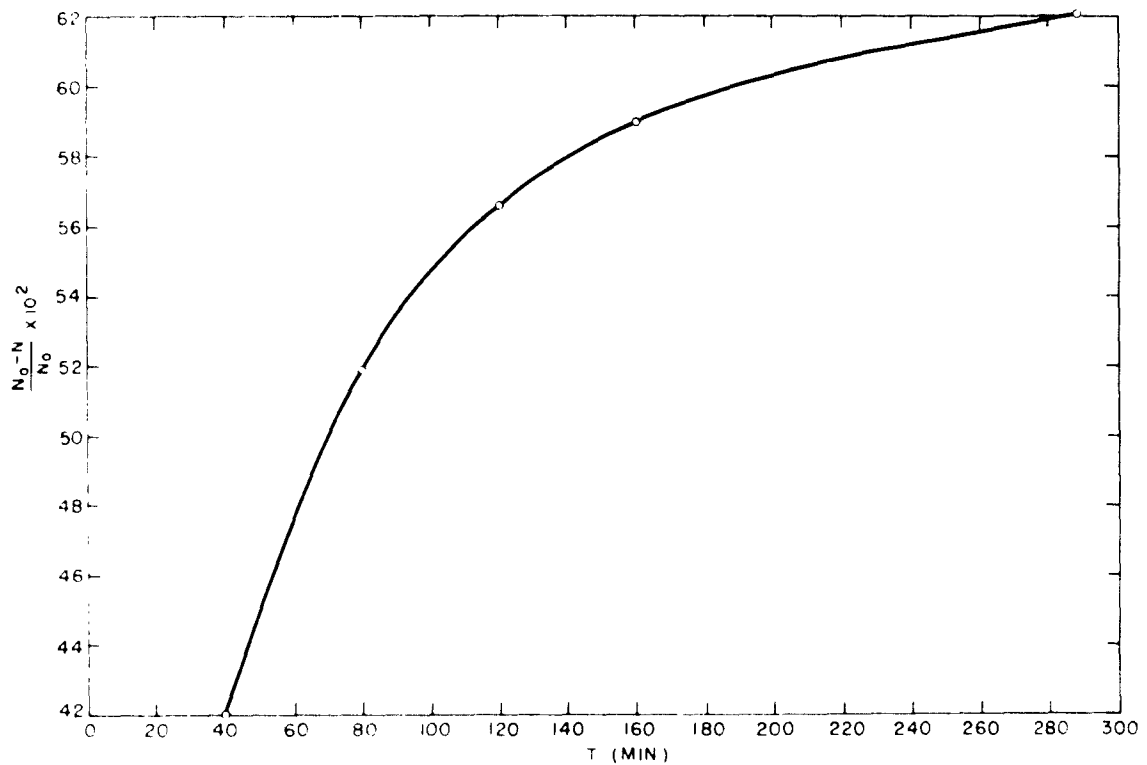
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FIG. 17 THERMAL DECOMPOSITION OF "EASTMAN
KODAK NITROGUANIDINE CRYSTALS" AT 189°C



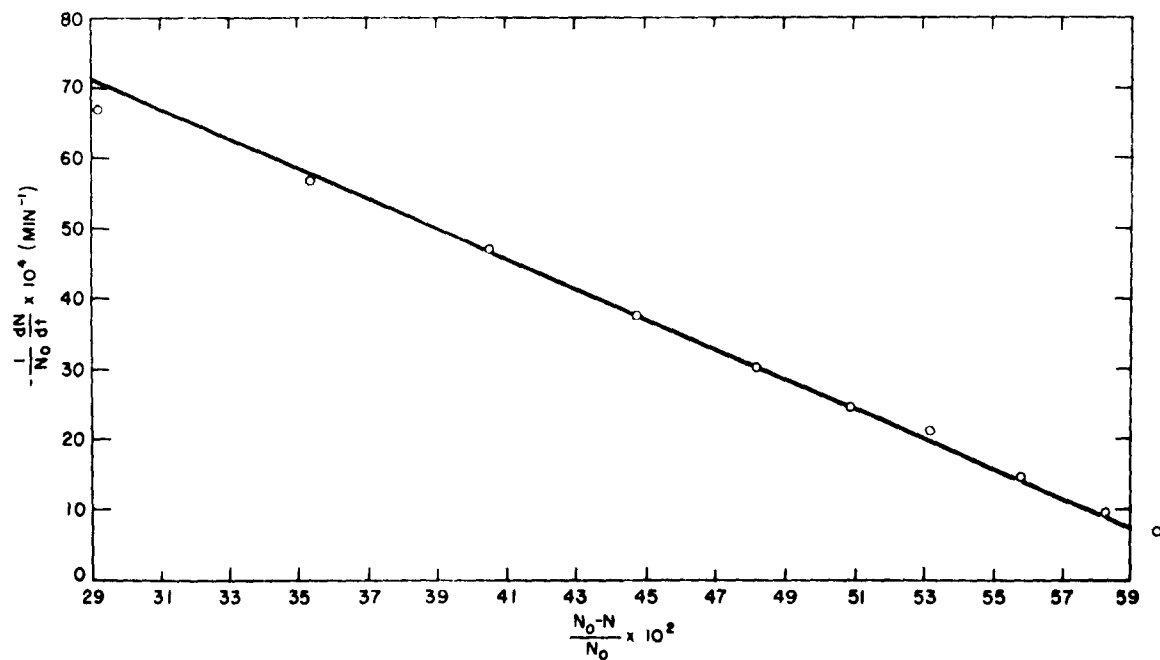
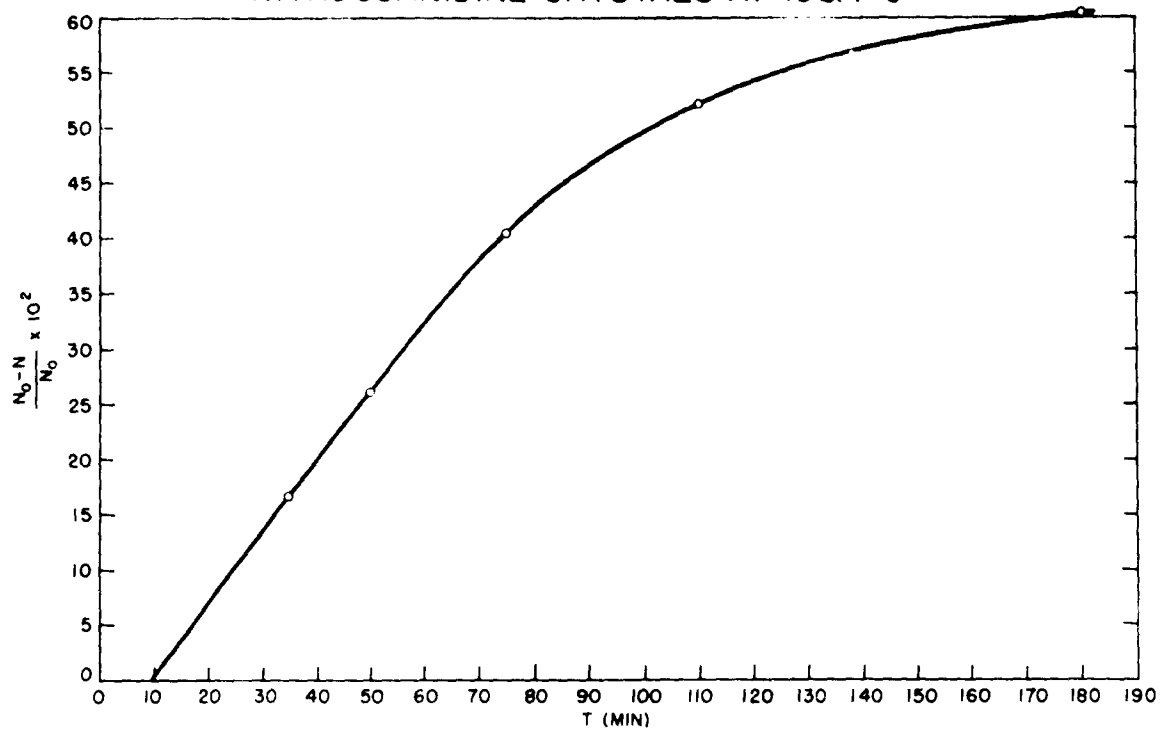
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FIG. 18 THE THERMAL DECOMPOSITION OF "NEEDLE-LIKE
NITROGUANIDINE CRYSTALS" AT 189°



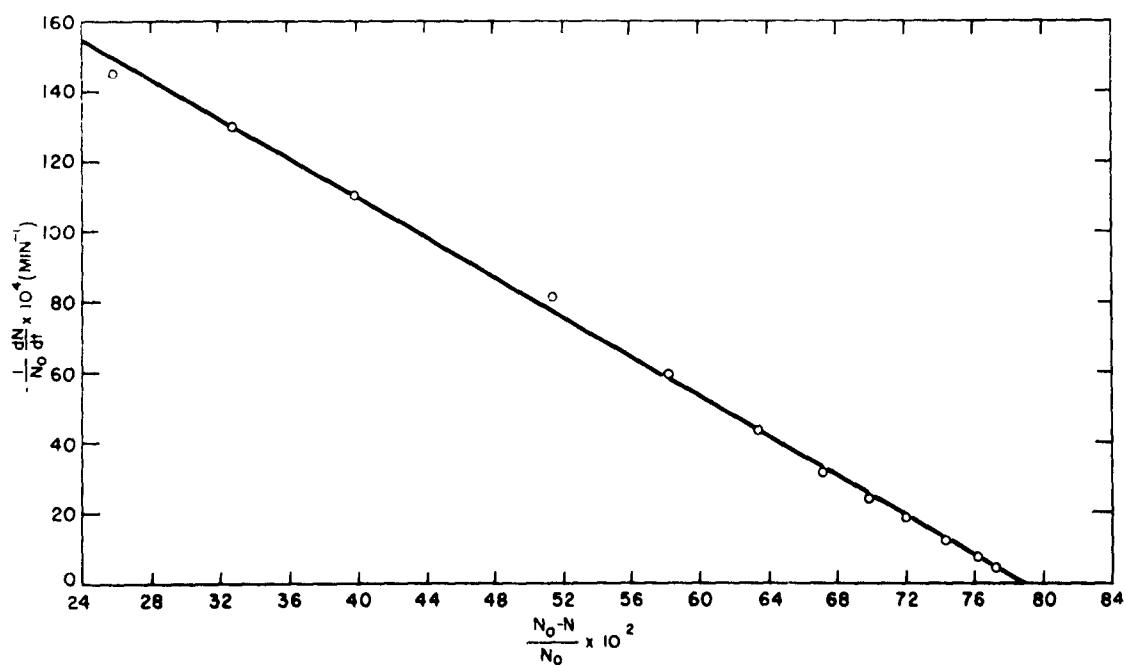
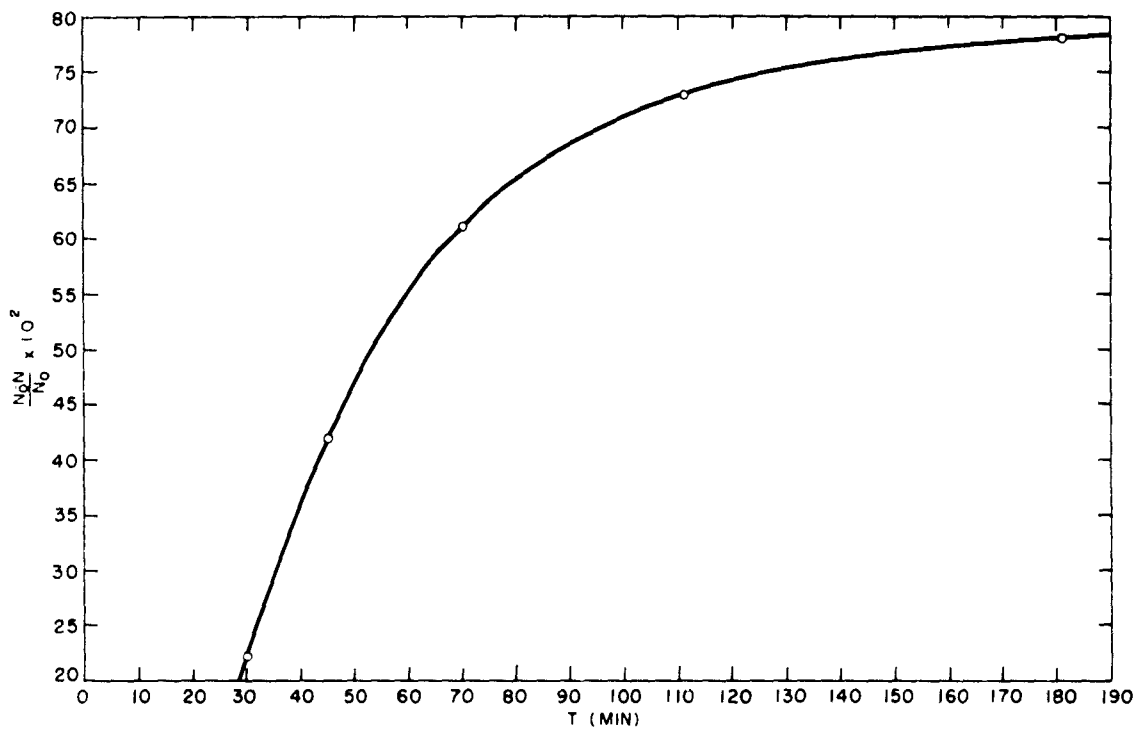
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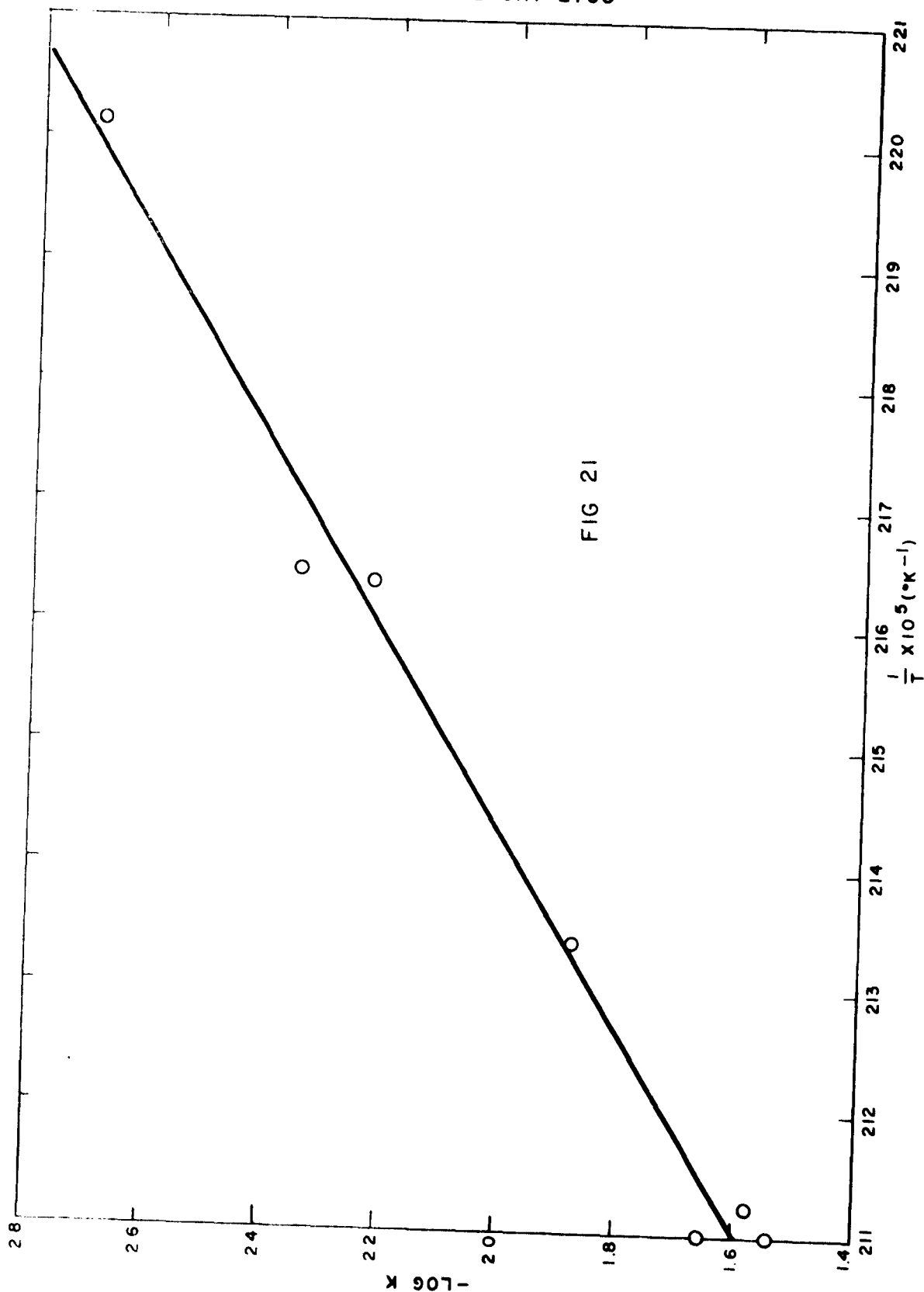
FIG. 19 THERMAL DECOMPOSITION OF "GROUND
NITROGUANIDINE CRYSTALS" AT 195.4° C



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FIG. 20 THERMAL DECOMPOSITION OF "GROUND
NITROGUANIDINE CRYSTALS" AT 200°C





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a. 0% DECOMPOSITION



b. 5% DECOMPOSITION



c. 15% DECOMPOSITION

FIG. 22 PHOTOMICROGRAPHS OF "GROUND NITROGUANIDINE CRYSTALS"
AT VARIOUS STAGES OF THERMAL DECOMPOSITION

THE MAGNIFICATION IS 1100X

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a. 30% DECOMPOSITION



b. 60% DECOMPOSITION

FIG. 23 PHOTOMICROGRAPHS OF "GROUND NITROGUANIDINE
CRYSTALS" AT VARIOUS STAGES OF THERMAL DECOMPOSITION.
THE MAGNIFICATION IS 1100X